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Aerosol Formation from Diesel Exhaust and SO2
A Chamber Study

Calspan Advanced Technology Center
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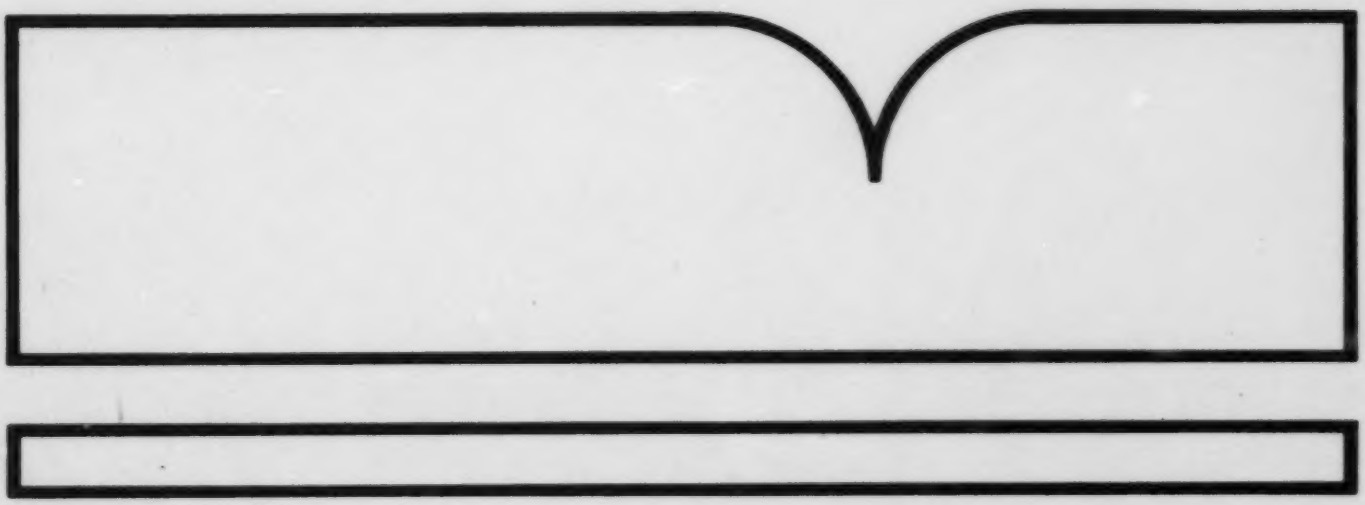

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16. ABSTRACT

Dilute diesel emission systems were studied in a 600 m^3 indoor smog chamber under various conditions likely to be encountered in an urban environment. Aerosol formation and growth in an irradiated diesel emission/SO_2/propylene system was primarily attributed to sulfate formation. During irradiated experiments, the rate of SO_2 oxidation experienced a maximum of about 5% hr^{-1} in the period when the O_3 concentration was increasing rapidly. Following the peak in the O_3 concentration, the rate of SO_2 oxidation decreased to about 1% hr^{-1}. The presence of the primary diesel aerosol appeared to increase the rate of SO_2 oxidation and the amount of aerosol sulfate formed as well as minimize the formation of new aerosols in irradiated experiments. In most irradiated experiments, the production of organic and nitrate aerosols represented minimal contributions to aerosol formation and growth.

The results of the Ames tests were as follows: (1) UV irradiation produced no significant changes, (2) UV irradiation in conjunction with ozone production decreased mutagenicity and resulted in a change in mutagen type demonstrated by increases in direct acting response over that requiring metabolic activation, (3) dark reaction of the exhaust gas with the aerosols resulted in increased mutagenicity, both with and without metabolic activation.

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*Exhaust emissions		21B
*Photochemical reactions		07E
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A Chamber Study

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ABSTRACT

Dilute diesel emission systems were studied in a 600 m^3 indoor smog chamber under various conditions likely to be encountered in an urban environment. The major emphases of the study were aerosol formation and growth, chemical kinetics, and the mutagenic activity of the diesel aerosol. Important parameters with respect to visibility degradation and the formation of new aerosol material included relative humidity, SO_2 concentration, HC/NO_x ratio, irradiation interval, and the presence of the primary diesel aerosol (primarily soot).

Aerosol formation and growth in uv-irradiated diesel exhaust/SO_2/propylene experiments were attributed to sulfate aerosol formation primarily. During the experiments, the rate of SO_2 oxidation to form sulfate aerosol was 5% hr^{-1} maximum during the O_3 production period. After the peak ozone production period, the first 3 to 6 hours of a 24-hour experiment, the ozone concentration remained relatively constant and the SO_2 oxidation rate decreased to approximately 1% hr^{-1}. These observations could be tentatively attributed to the SO_2/hydroxyl radical reaction during the initial hours of the experiments. The hydroxyl radical concentration is high during the first few hours of ozone production and the gas phase SO_2/hydroxyl reaction predominates.

The effect of the primary diesel aerosol on new particle formation was investigated by conducting experiments with and without prefiltered diesel exhaust. The presence of diesel aerosols precluded the formation of new aerosol particles; instead the existing aerosols grow in diameter by the condensation of nuclei on them. The presence of the primary diesel aerosols appeared to increase the rate of SO_2 oxidation and the amount of sulfate formed via unknown heterogeneous or catalytic reactions. Increases in aerosol sulfate of from 25 to 75 percent were attributed to the presence of the primary diesel aerosol in contrast to what was attributed to the SO_2/hydroxyl radical gas phase reaction.

In most irradiated experiments, the production of organic and nitrate aerosols represented minimal contributions to aerosol formation and growth. Nitrate aerosols (>1000 $\mu g/m^3$) did represent a substantial fraction of the total aerosol growth in an experiment in which NH_3 was added to the system.

The mutagenic activity of the diesel aerosol was observed to be affected by simulated atmospheric exposure. Containment of dilute diesel emissions under non-irradiated conditions resulted in an increase in the mutagenic activity of the diesel

aerosol. While irradiation per se appeared to have no effect upon the mutagenic activity, photochemically reactive systems exhibited decreases in mutagenic activity of the diesel aerosols with irradiation. At least a portion of the observed decrease in mutagenicity was attributed to the presence of O_3 (a product of the photochemistry).

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NOMENCLATURE

B_{scat} = Light Scattering Coefficient

CCN = Cloud Condensation Nuclei

CVS = Constant Volume Sampler

E = elemental carbon

HC = hydrocarbon

IC = ion chromatography

LWC = liquid water content

N = nitrate

O = organic carbon

RH = Relative Humidity

R_{SO_2} = Rate of SO_2 Oxidation:

$$\left[\frac{2/3\ \Delta\text{sulfate}}{(\text{available } SO_2)_{\text{average}} \cdot \Delta\text{time}} = R_{SO_2}\right]$$

S = sulfate

w/ = with

w/o = without

x_i = initial value of x

XRF = wave-length dispersive x-ray fluorescence

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Section 1
INTRODUCTION

Auto exhaust emissions represent one of the most ubiquitous anthropogenic pollution sources. Especially within the past decade, a significant quantity of research has been devoted to studies of the impact of the emissions of gasoline-fueled autos upon the health of man and the environment, the formation of smog, and the composite levels of various pollutants. These investigations have provided data upon which both federal and state control strategies are based. During this period, the use of light duty diesel-fueled autos in the United States was insignificant as indicated by the fact that light duty autos used almost 10^4 times by volume more gasoline than diesel fuel in the United States during 1976. Total on-highway diesel fuel usage was about 10% by volume of the amount of gasoline used (Office of Technology Assessment, 1977). While the level of usage of heavy duty diesel-fueled vehicles was not easily neglected, such vehicles were generally routed around major urban areas to the extent that their contribution to the urban pollution problem was comparatively small.

With the relatively recent escalation in the price of fuel for autos, an economic justification has evolved for the use of light duty diesel-fueled autos. Presently, several foreign auto makers and at least one domestic auto maker offer such vehicles. It is speculated that light duty diesels could comprise 25% of the new car fleet by 1985. With the potential for such a dramatic increase in the use of light duty diesel-fueled autos as well as the development of medium duty diesels, it is necessary that investigations begin to anticipate the impact of such levels of diesel emissions upon urban pollution levels (both particulate and gaseous), photochemical and catalytic oxidation processes responsible for significant rates of gas-to-particle conversion in the urban atmosphere, and the health of the urban population.

As a result of the significant differences between diesel and gas-fueled auto emissions and the potential for widespread use of diesels in the near future, smog chamber studies of a simulated diesel exhaust/urban system were performed by Calspan Corporation under Contract No. 68-02-2987 from the U.S. Environmental Protection Agency. The program, which was performed in Calspan's 600 m^3 indoor smog chamber, was aimed at assessing the role of diesel emissions in future urban environments. The experiments provided semi-quantitative data on aerosol formation and growth, chemical kinetics, and the evolution of mutagenicity in the diesel exhaust/SO_2/hydrocarbon system.

With respect to gasoline-fueled autos, the emissions of light duty diesels generally contain comparable ratios of gaseous hydrocarbons to oxides of nitrogen, and high levels of known or suspected mutagens. Diesel emissions also contain copious quantities of primary particulates (soot). Of particular concern to this study was the role of the large quantities of primary particulates contained in the diesel emissions upon the physical and chemical nature of the urban atmosphere. Experimental evidence (Novakov et al, 1974; Barbaray et al, 1977; and Tartarelli et al, 1978) indicates that carbonaceous particles may represent active sites for the catalytic oxidation of SO_2, thus resulting in increased levels of particulate sulfate. In addition, the presence of primary particulates may contribute significantly to the urban aerosol load.

Also condensed on primary particulates are the high molecular weight organics which contribute to the known mutagenicity of diesel emissions. The fate of these compounds in the urban atmosphere is uncertain. A recent study (Pitts et al, 1978) has shown that benzo (a) pyrene and other polycyclic aromatic hydrocarbon promutagens may be converted to direct-acting mutagens by exposure to simulated smog conditions. On the other hand, polycyclic aromatic hydrocarbons are strong absorbers in the ultra-violet spectrum and may be susceptible to photolysis under exposure to irradiation in the atmosphere.

To simulate the urban system, hydrocarbons and SO_2 were added to diluted diesel emissions. Initially, the spiked hydrocarbons consisted of a combination of propylene and butane or propylene alone. Later experiments utilized a mixture of diesel and gasoline-fueled auto emissions to more

accurately simulate the urban system. The smog chamber tests were performed for a variety of conditions. Varied parameters included RH, irradiation, SO_2, HC/NO_x, and the concentration of primary diesel exhaust particulates.

A detailed discussion of the results of these experiments is presented in Section 4 and specific details of aerosol formation and growth are discussed in Section 5. Results of investigations of the mutagenic activity of diesel aerosols before and after exposure to simulated urban atmospheres are presented in Section 6. Aerosol, gas, and filter analyses data for these experiments, where available, are presented in Appendix A. Appendix B presents aerosol mass loading values, obtained at the end of each experiment, as determined by three independent techniques. A description of the experimental facilities and equipment necessary to perform this investigation of diesel emission systems may be found in Appendix C. Brief summaries of the principal conclusions and recommendations derived from this study may be found in Sections 2 and 3.

Section 2
CONCLUSIONS

The high level of primary particulates (soot) and the condensed high molecular weight organics were the major differences between the diesel emission/SO_2/hydrocarbon* system studied in this program and the hydrocarbon/NO_x/SO_2 systems which have been studied in other programs, including a recent Calspan study of the photochemistry of gasoline-fueled auto emission systems (Anderson et al, 1979). Qualitatively, the photochemical reactivities of the system (in terms of NO decay, O_3 formation, etc.) were very similar. Significant differences did exist between the gasoline-fueled auto emission and diesel emission systems in terms of the effects of primary particulates upon sulfate formation. In the previous program, we observed that the primary particulates of gasoline-fueled auto emissions did not measurably influence the oxidation of SO_2 under irradiated conditions. As is discussed below, in the present program an increased rate of SO_2 oxidation due to the primary particulates of the diesel emissions was detected. It is not known whether this difference was due to the greater concentration of the diesel aerosol with respect to the primary particulates of the gasoline-fueled auto emissions or was due to a unique chemical or physical character of the diesel primary aerosol. The greater concentration of the diesel primary aerosol also reduced the formation of secondary aerosols.

For UV-irradiated tests, the activity of the diesel emission/SO_2/propylene system (with respect to aerosol formation and growth) had three distinct levels which correlated well with the rate of change of ozone concentration with time. Although new particle formation was frequently associated with the initiation of irradiation, the rate of increase in aerosol volume remained

*The concentration of gaseous hydrocarbons contained in diesel emissions was too low to significantly influence the systems photochemistry - hence the need to add a reactive hydrocarbon (propylene).

relatively low until substantial amounts of nitrogen dioxide were formed by the oxidation of nitric oxide. The ozone concentration was very low during this period (< 10 ppb). Following an increase in the concentration of nitrogen dioxide, the ozone concentration began to increase. This period of increasing ozone concentration represented the most active portion of the experiment for aerosol growth. Since there generally were sufficient particles to serve as sites for condensation of the new matter, few new particles were formed. The final level of system activity occurred after the ozone peak, which generally coincided with the depletion of propylene (the predominant reactive hydrocarbon species). Subsequent to the ozone peak, there was a gradual but persistent decay in the ozone concentration. Little further aerosol growth or visibility degradation was associated with this period.

Aerosol formation and growth in the diesel emission/SO_2/propylene system was primarily due to sulfate formation. Prior to the period of rapidly increasing ozone (during the decay of nitric oxide), SO_2 oxidation rates (R_{SO_2}) on the order of 0.1% hr^{-1} were observed. SO_2 oxidation rates were determined from measured increases in aerosol sulfate with time and the concentration of available SO_2. During the period of increasing ozone concentration, R_{SO_2} generally approached 5% hr^{-1}. Subsequent to the formation of the ozone peak, R_{SO_2} decreased to a low value (< 1% hr^{-1}) and occasionally was undetectable due to losses of sulfate aerosols in excess of the rate of formation of sulfate. Such aerosol losses were due to sedimentation and diffusion to the chamber walls. The fact that sulfate formation was greatly reduced, even though ozone and SO_2 continued to coexist, provided evidence that the SO_2-ozone reaction was not the primary path for sulfate formation during the period of high R_{SO_2}. Comparisons of aerosol sulfur as determined by IC (soluble sulfate) and XRF (total elemental sulfur) demonstrated good agreement, indicating that the concentration of sulfonated organics was small with respect to total sulfates.

The primary particulates of the diesel emissions were principally composed of elemental carbon and various condensible organic compounds. Analyses of the primary particulates of diluted diesel emissions revealed an elemental to organic carbon ratio of about 5 to 1. One of the major effects of the primary particulates was to increase the mass median diameter (MMD) of

the aerosol (e.g., 0.3 to 0.4 μm) through a redistribution of mass versus particle size. As a result, the presence of primary particulates yielded an increased effectiveness of the aerosol to scatter light. The increased MMD might be indicative of an increasing fraction of material deposited deep within the human lungs during respiration, as a larger portion of the individual aerosol particles falls within the respirable size range (0.5 to 3 μm diameter).

Greater quantities of aerosol sulfate were consistently produced by irradiated systems containing the primary diesel aerosol than by comparable systems which did not contain the primary diesel aerosol. While the actual quantity of increased sulfate was difficult to assess (due to few duplicate experiments), increases in aerosol sulfate of from 25 to 70 percent were attributed to the primary particulates. This apparent increase in sulfate formation may have been due to heterogeneous reactions on the surface of the carbonaceous particles or may have been associated with the high molecular weight organics known to be carried by the primary aerosols of the diesel exhaust. No significant sulfate formation was observed in the non-irradiated diesel exhaust/SO_2/hydrocarbon system at low humidity. However, at high humidities ($\sim$ 92%) SO_2 oxidation rates as high as 1.5% hr^{-1} were observed under dark conditions. To minimize error in the measurement of the SO_2 concentration, the analyzer was calibrated at the beginning of each experiment using carrier air with the same RH as that to be encountered in the experiment.

In irradiated diesel emission/SO_2/hydrocarbon systems, aerosol nitrate concentrations of about 1 $\mu g/m^3$ (approximately the blank level of the filter) and gaseous ammonia concentrations of <10 ppb were typically observed. With the introduction of ozone at low RH (<80 %) into the system, the concentration of aerosol nitrate appeared to increase temporarily. At high humidity (94%), significant aerosol nitrate was formed ($\sim$30 $\mu g/m^3$) and persisted with the introduction of ozone. Aerosol nitrate represented a substantial fraction of total aerosol growth in only one experiment (where 10 ppm of NH_3 had been added to the chamber). The reaction of NH_3 with gaseous nitric acid to produce the more stable ammonium nitrate apparently was responsible for the presence of a significant concentration of aerosol nitrate (in excess of 1000 $\mu g/m^3$) in this particular experiment.

From many of the experiments, hi-vol aerosol samples typically weighing several tenths of a gram were collected for analysis by the standard Ames' test. These tests determined the mutagenicity of the diesel exhaust aerosol and provided data on the changes in mutagenicity due to the effects of exposure of diesel exhaust aerosol to an urban environment. This survey-type effort identified two conditions which appeared to influence the mutagenicity of diesel emissions. With respect to the initial mutagenic activity of the diesel emissions, aging in the dark tended to result in higher mutagenic activity while exposure to ozone appeared to reduce the mutagenic activity. Irradiation per se did not appear to affect the mutagenic activity of the diesel aerosol. These findings were not quantified, and it is likely that we did not identify all of the atmospheric mechanisms or conditions in which the mutagenic activity of diesel emissions will be modified.

Section 3
RECOMMENDATIONS

This program was wide-ranging in scope and, as a result, survey-type in nature. The goals of the program were to identify potential problem areas associated with diesel emissions in an urban atmosphere and isolate specific parameters responsible for or contributing to these potential problems. Noted trends which warrant further study are discussed below.

Most of the significant trends noted in these tests of the diesel emission/SO_2/hydrocarbon system were associated with the primary particulates of the diesel emissions. The primary particulates are apparently responsible for an increase in the amount of sulfate formed during irradiated tests and during high humidity conditions in the absence of irradiation. Further experiments should be performed to quantify the expected increase in sulfate versus the loading of primary particulates. Experiments should also be performed to identify the component of the primary particulates responsible for the increased sulfate formation (i.e., the carbon or the organics).

The experiments performed on this program concentrated on simple systems (i.e., the addition of propylene and butane to diluted diesel emissions) to simulate the diesel emission/urban atmosphere. This system was chosen initially to aid in modeling the observed photochemistry. Only a limited number of experiments were performed with a more representative mixture of diesel and gasoline-fueled engine emissions. While the photochemical reactivities of the simple and more complex systems are similar, there are definite differences in specific aspects of the systems. For example, the simple diesel emission/reactive hydrocarbon system exhibits a very low rate of sulfate formation following the ozone peak. The more complex diesel/gasoline-fueled engine emission system (approximately 30 percent of total diluted emissions were diesel) does not exhibit such a sharp dependence of sulfate formation on the formation of the ozone peak. To assure

optimum relevance of experimental data, future experiments should be performed with the more representative diesel/gasoline-fueled engine emission system.

The potential for nitrates to contribute substantially to aerosol formation and growth in the presence of high NH_3 concentrations has been demonstrated. Further investigations are in order to determine the role of NH_3 and liquid water in promoting the formation of aerosol nitrate from an apparently abundant source of gaseous nitrates.

This program only began to explore the possible effects of age and atmospheric exposure upon the mutagenicity of diesel aerosols. Many questions pertaining to the mutagenicity of diesel aerosols and aerosols in general, remain unanswered. These questions concern: the chemical species responsible for the mutagenicity of diesel emissions; the effects of irradiation upon specific mutagenic compounds; the overall lifetime of mutagenic materials in the atmosphere; mechanisms for the elimination of mutagenic compounds in the atmosphere; potential mechanisms by which mutagenic compounds may be formed by atmospheric reactions; and, the mutagenicity of gaseous constituents of diesel emissions. With the potential for an increasing atmospheric burden of mutagenic aerosols to adversely affect the public health, basic studies should be performed to determine the lifetimes and possible formation mechanisms of mutagenic compounds in the atmosphere.

Section 4
EXPERIMENTAL RESULTS

In recent years, a significant level of effort has been devoted to the study of the chemical and physical processes responsible for smog formation in urban environments. Experimental data provided by field and laboratory measurements have allowed many of the more important parameters to be identified and modeled. As a result, current photochemical kinetic models generally provide at least the qualitative trends observed experimentally. As new systems become important, they must be studied experimentally to assure that they are adequately described by existing models.

One of the primary differences between the emissions of light duty diesels and gasoline-fueled, catalyst-equipped autos is the copious quantity of diesel primary particulates (soot). In a past EPA-sponsored program (Anderson et al, 1979), we observed that the primary particulates of gasoline-fueled auto emissions did not contribute significantly to SO_2 oxidation with respect to standard photochemical processes. One of the purposes of the current program was to investigate the influence of the primary particulates of the diesel emissions upon the rate of gas-to-particle conversion. If the primary particulates do significantly influence the photochemical reactions of the system, existing models will not provide an accurate assessment of the system.

Condensible organics known to be mutagenic are also associated with the primary particulates of the diesel emissions. Another aspect of this program was to investigate the fate of these organics under various simulated conditions to determine if the mutagenicity of the emissions is likely to be modified with exposure to an urban environment.

This experimental study of the diesel emission/hydrocarbon system was performed to assess the physical and chemical nature of the system. Particular interest was vested in the primary particulates of the diesel emissions and their influence upon the system. The mutagenic nature of the aerosol and its evolution with exposure to various conditions (i.e., irradiation, high relative humidity, high O_3, etc.) were also studied.

PRESENTATION AND OVERVIEW OF THE DATA

In an effort to provide an overview of the diesel exhaust/SO_2/ hydrocarbon system, a series of experiments was performed to study aerosol formation and growth, the chemical kinetics, and the evolution of mutagenicity in the system under a variety of simulated urban conditions. A complete log of all of the experiments (60) performed on the program is presented in Table 1. The log contains a descriptive experiment title, specifics of the procedure used in handling the emissions, initial conditions in the chamber (including initial gas concentrations), the maximum O_3 concentration, initial added concentration of hydrocarbons (propylene and butane), the time required to reach the O_3 peak, and the weight and age of the hi-vol sample. Aerosol, gas, and filter analyses data for these experiments, where available, are presented in Appendix A. Appendix B presents aerosol mass loading values, obtained at the end of each experiment, as determined by three independent techniques. Results of investigations of the mutagenic activity of diesel aerosols before and after exposure to simulated urban atmospheres are presented in Section 6. A description of the experimental facilities and equipment necessary to perform this investigation of diesel emission systems may be found in Appendix C.

Several classes of experiments were performed. Among these, routine experiments provided a determination of the dilution ratio of the auto emissions in the smog chamber while measurements of the light intensity of the irradiation system were performed on a regular basis. With the concentration of the primary particulates of the diesel emissions beyond the range of our aerosol characterization devices ($\gtrsim$600 $\mu g/m^3$), some experiments were devoted to obtaining large quantity aerosol samples for mutagenic testing. The majority of experiments were aimed at assessing aerosol formation and growth

TABLE 1. LOG OF EXPERIMENTS

Experiment	Date	Exp.† Proc.	Driving†† Cycle	Auto**	$T(^{\circ}C)_i$	$RH(\%)_i$	Irrad.	Vis_{by_i} (km)	$Aitken_i$ ($\#/cm^3$)	Gases (ppm) SO_{2_i}	NO_i	NO_{2_i}	O_{3_i}	$O_{3_{max}}$	Spiked HC (ppmC) Prop.	Butane	Time to O_3 Peak	Hi-Vol Sample (g)	Sample Age (hrs)
1. Diesel Exhaust Mutagenic Background	2/5/79	C/0	UDC	M	14.4	82	–	0.10	–	0.52	*	*	<.001	<.001	–	–	–	0.62	0.5
2. Diesel Exhaust Irradiated Mutagenic	2/6/79	C/0	UDC	M	16.7	79	I	0.10	–	0.56	*	*	<.001	<.001	–	–	>6 hrs	0.63	6.0
3. Diesel Exhaust Aged Mutagenic	2/16/79	C/0	UDC	M	17.2	80	–	0.10	2.5×10^5	0.61	4.10	0.50	<.001	<.001	–	–	–	0.63	6.0
4. Diesel Exhaust Irradiated Mutagenic	2/18/79	C/0	UDC	M	17.8	85	I	0.10	2.4×10^5	0.58	3.90	0.80	<.001	<.001	4.5	12	>6 hrs	0.67	6.0
5. Light Intensity Test Scratched	2/20/79	–	–	–	18.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–
6. Prop/SO_2/NO_x	2/20/79	–	–	–	18.1	80	I	80	7.3×10^4	0.37	0.24	0.08	<.001	0.110	3.0	–	>3.5 hrs	–	–
7. Light Intensity $k_d = 0.21\ min^{-1}$	2/21/79	–	–	–	16.7	44	I	–	–	–	0.01	1.47	<.001	0.09	–	–	30 sec	–	–
8. Diesel Exhaust Dilution Test	2/27/79	C/1	FET	M	17.2	68	–	1.00	9.5×10^4	0.31	2.1	0.15	<.001	<.001	–	–	–	–	–
9. Light Intensity $k_d = 0.21\ min^{-1}$	2/27/79	–	–	–	16.9	39	I	–	–	–	<0.01	0.73	<.001	0.05	–	–	30 sec	–	–
10. Diesel Exhaust Dilution Test	2/27/79	C/4	FET	M	16.9	68	–	3.20	1.1×10^5	0.13	0.88	0.03	<.001	<.001	–	–	–	–	–
11. Diesel Exhaust Test Scratched	2/28/79	C/0	FET	M	17.8	85	–	0.10	1.4×10^5	0.43	3.1	0.30	<.001	<.001	–	–	–	–	–
12. Diesel Exhaust w/o primary part.	3/1/79	C/4, A(60)	FET	M	17.5	68	I	80	900	0.03	0.54	0.06	<.001	0.015	1.5	4.0	>6 hrs	0.02	6.0
13. Diesel Exhaust Mutagenic Background	3/2/79	C/0	FET	M	17.2	91	–	0.12	1.7×10^5	0.56	3.0	0.30	<.001	<.001	–	–	–	0.51	0.5
Wash Chamber	3/3/79																		
14. Diesel Exhaust Partial Aerosol Filt.	3/6/79	C/4, A(10)	FET	Da	17.2	78	I	17.0	4.0×10^4	–	0.77	0.04	<.001	0.007	1.5	4.0	>6 hrs	0.05	6.0
15. Diesel Exhaust Mutagenic Background	3/7/79	C/0	FET	Da	17.5	66	–	0.17	1.9×10^5	0.37	3.75	0.38	<.001	<.001	–	–	–	0.51	0.5
16. Diesel Exhaust Partial Aerosol Filt.	3/8/79	C/4, A(10)	FET	Da	17.5	77	I	11.0	5.5×10^4	1.05	0.69	0.03	<.001	0.009	1.5	4.0	>6 hrs	0.09	6.0
17. Diesel Exhaust Diluted/ Irrad.	3/9/79	D(61)	FET	Da	17.5	38	I	22.4	4.5×10^3	0.53	0.20	0.07	<.001	0.16	1.5	–	>6 hrs	–	–
18. Diesel Exhaust	3/12/79	D(45)	FET	Da	16.7	20	I	9.2	1.0×10^5	0.85	0.46	0.11	<.001	0.09	1.5	4.0	>24 hrs	0.13	24.0
19. Diesel Exhaust increase propylene	3/14/79	D(45)	FET	Da	18.0	35	I	8.8	1.1×10^5	0.67	0.53	0.11	<.001	0.44	3.0	2.0	19 hrs	0.30	24.0
20. Light Intensity $k_d = 0.30\ min^{-1}$	3/15/79	–	–	–	18.6	18	I	–	–	–	<0.01	0.72	<.001	0.07	–	–	30 sec	–	–
21. Diesel Exhaust Hot Emission Filt.	3/16/79	F, D(61)	FET	Da	16.9	20	I	25.8	3.5×10^3	0.55	0.20	0.07	<.001	0.50	3.0	–	4.5 hrs	0.27	6.0
22. Diesel Exhaust Repeat #19	3/18/79	D(45)	FET	Da	17.5	37	I	8.9	1.0×10^5	0.65	0.49	0.12	<.001	0.50	3.0	2.0	11 hrs	0.36	24.0
23. Diesel Exhaust Repeat #14	3/20/79	C/4, A(10)	FET	Da	17.8	76	I	9.6	5.3×10^4	0.11	0.85	0.03	<.001	0.003	1.5	4.0	>6 hrs	0.08	6.0
24. Diesel Exhaust Repeat #16	3/21/79	C/4, A(10)	FET	Da	17.8	78	I	10.9	6.9×10^4	0.09	0.84	0.04	<.001	0.002	1.5	4.0	>6 hrs	0.10	6.0
25. Diesel Exhaust	3/22/79	D(61)	FET	Da	18.3	37	I	22.4	4×10^3	0.55	0.22	0.07	<.001	0.47	3.0	–	4 hrs	0.23	24
Wash Chamber	3/23/77																		

TABLE 1. (continued)

Experiment	Date	Exp.† Proc.	Driving†† Cycle	Auto**	$T(^{o}C)_i$	$RH(\%)_i$	Irrad.	Vis_{by_i} (km)	$Aitken_i$ ($\#/cm^3$)	Gases (ppm) SO_{2_i}	NO_i	NO_{2_i}	O_{3_i}	$O_{3_{max}}$	Spiked HC (ppmC) Prop.	Butane	Time to O_3 Peak	Hi-Vol Sample (g)	Sample Age (hrs)
26. Diesel Exhaust w/o primary part.	3/26/77	F, D(46), A(28)	FET	Da	16.7	26	I	80	800	0.52	0.44	0.12	<.001	0.36	3.0	2.0	13 hrs	0.22	24
27. Light Intensity Test Scratched	3/27/79	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
28. Prop/SO_2/NO_x	3/28/79	–	–	–	17.5	19	I	80	2.7×10^4	0.52	0.20	0.22	*	*	3.0	–	*	0.22	6.0
29. Prop/SO_2/NO_x	3/29/79	–	–	–	18.9	44	I	80	5.8×10^4	0.47	0.30	0.05	<.001	0.43	3.0	2.0	8 hrs	0.14	24
30. Diesel Exhaust GCMS Samples	6/1/79	D(10)	FET	M	24.8	97	–	0.12	–	–	–	–	–	–	–	–	–	0.73	0.5
Replace Lamps in Irradiation System	6/4/79																		
Wash Chamber	6/26/79																		
31. Light Intensity $k_d = 0.8\ min^{-1}$	6/27/79	–	–	–	24.8	59	I	–	–	–	<0.01	0.72	<.001	0.15	–	–	30 sec	–	–
Irrad. System Aged ~24 hrs																			
32. Diesel Exhaust Double Aerosol Samples	6/29/79	U	FET	M	15.0	72	–	0.07	1.7×10^5	0.89	>5.0	1.1	<.001	<.001	–	–	–	0.86 0.77	0.5 6.0
33. Diesel Exhaust High O_3	7/2/79	C#4	FET	M	21.1	71	–	–	1.9×10^5	0.21	<.001	0.65	0.69	0.89	–	–	–	0.22	6.0
34. Diesel Exhaust Exhaust & Hi-Vol Aerosol Samples	7/3/79	F	FET	M	22.1	67	–	0.27	3×10^5	1.10	>5.0	1.0	*	*	–	–	–	0.43	0.5
35. Diesel Exhaust High RH; High O_3	7/4/79	C#4	FET	M	21.9	94	–	0.75	4.5×10^5	0.97	0.88	0.06	<.001	0.75	–	–	O_3 added after 3 hrs	–	–
36. Diesel Exhaust	7/5/79	C#4, D(15)	FET	M	19.4	41	I	16.0	2.5×10^4	0.60	0.20	0.04	<.001	0.012	3.0	–	>6 hrs	0.09	6.0
37. Diesel Exhaust Add 3.5 ppmC Toluene	7/6/79	C#4, D(25)	FET	M	18.9	53	I	21.7	2.2×10^4	0.60	0.09	0.10	<.001	0.24	–	–	6 hrs	0.24	6.0
38. Diesel Exhaust w/o primary part.	7/9/79	F, C#4, D(25), A(38)	FET	M	26.6	51	I	80	3.7×10^3	0.54	0.06	0.10	<.001	0.51	3.0	–	2 hrs	–	–
39. Light Intensity $k_d = 0.59\ min^{-1}$	7/9/79	–	–	–	29.7	46	I	–	–	–	<0.01	0.52	<.001	0.15	–	–	30 sec	–	–
40. Diesel Exhaust Low SO_2	7/10/79	C#4, D(25)	FET	M	26.7	57	I	19.3	5.0×10^4	0.056	0.06	0.09	<.001	0.54	3.0	–	2 hrs	0.88	6.0
41. Diesel Exhaust High RH	7/11/79	C#4, D(25)	FET	M	25.6	91	I	10.6	3.8×10^4	0.37	0.09	0.07	<.001	0.42	3.0	–	2 hrs	–	–
42. Light Intensity $k_d = 0.55\ min^{-1}$	7/11/79	–	–	–	28.5	65	I	–	–	–	<0.01	0.95	<.001	0.13	–	–	30 sec	–	–
43. Diesel Exhaust	7/12/79	C#4, D(25)	FET	M	25.9	63	I	16.1	4.3×10^4	0.56	0.09	0.08	<.001	0.53	3.0	–	2 hrs	0.15	6.0
44. Diesel Exhaust Double Aerosol Samples	7/13/79	U	FET	M	27.2	56	I	*	2×10^5	1.2	>5.0	*	*	*	–	–	*	0.38 0.86	0.5 6.0
45. Diesel Exhaust Dilution Test	10/18/79	P(40)	FET	M	–	–	–	–	–	0.85	–	–	–	–	–	–	–	–	–
46. Diesel Exhaust Dilution Test	10/23/79	P(10)	FET	M	–	–	–	–	–	0.20	0.55	–	–	–	–	–	–	–	–
47. Test Scratched	10/24/79	P(40)	FET	M,B	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
48. Test Scratched	10/24/79	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Wash Chamber	10/25/79																		

TABLE 1. (continued)

Experiment	Date	Exp.† Proc.	Driving†† Cycle	Auto**	$T(^{\circ}C)_i$	$RH(\%)_i$	Irrad.	$Vsby_i$ (km)	$Aitken_i$ ($\#/cm^3$)	Gases (ppm)					Spiked HC (ppmC)		Time to O_3 Peak	Hi-Vol Sample (g)	Sample Age (hrs)
										SO_{2_i}	NO_i	NO_{2_i}	O_{3_i}	$O_{3_{max}}$	Prop.	Butane			
49. Diesel/Gas Trial	10/26/79	P(40)	FET	M,B	16.6	52	I	–	1.0×10^5	0.05	>5.0	1.9	<0.001	0.001	–	–	–	–	–
50. Diesel/Gas	10/29/79	P(40), D(30)	FET	M,B	17.2	42	I	6.9	2.4×10^4	0.18	0.29	1.4	<0.001	0.024	–	–	–	–	–
51. Diesel/Gas	10/30/79	P(10), D(10)	FET	M,B	16.3	47	I	10.0	2.7×10^4	0.27	1.8	1.9	<0.001	0.001	6.0	–	–	0.09	0.0
52. Diesel/Gas	10/31/79	P(40)	FET	M,B	16.3	56	–	–	1.1×10^5	0.72	>5.0	1.8	<0.001	–	–	–	–	0.27	0.5
Double Aerosol Samples					16.9	51	–	–	2.7×10^4	0.52	4.0	3.4	<0.001	–	–	–	–	0.30	5.0
53. Diesel/Gas	11/1/79	P(40), D(30)	FET	M,B	19.2	42	I	6.9	2.3×10^4	0.56	0.42	1.2	<0.001	0.59	6.0	–	4 hrs	0.48	6.0
54. $SO_2 + O_3$ Dark Reaction	11/2/79	–	–	–	19.8	40	–	52	1.2×10^4	0.86	–	–	>1.0	–	–	–	–	–	–
55. Light Intensity $k_d = 0.48\ min^{-1}$	11/2/79	–	–	–	20.3	40	I	–	–	–	<0.01	1.2	<0.001	–	–	–	–	–	–
56. Diesel/Gas	11/5/79	P(40), D(30)	FET	M,B	19.2	35	I	23.3	2.5×10^4	0.04	0.83	1.2	<0.001	0.01	6.0	–	>6 hrs	0.24	6.0
57. Diesel/Gas	11/6/79	P(40), D(30)	FET	M,B	20.3	32	I	2.9	1.8×10^4	0.63	0.42	1.6	<0.001	0.60	6.0	–	3 hrs	0.69	6.0
58. Diesel/Gas w/o primary part.	11/7/79	P(40), D(30), A(60)	FET	M,B	18.1	43	I	50	1.0×10^5	0.61	0.43	1.2	<0.001	0.43	6.0	–	3½ hrs	0.32	6.0
59. Diesel/Gas with 10 ppm NH_3	11/8/79	P(40), D(30)	FET	M,B	19.3	28	I	3.4	–	0.56	0.50	1.7	<0.001	0.07	6.0	–	>6 hrs	0.88	6.0
60. Prop/SO_2/NO_x	11/9/79	–	–	–	16.1	42	I	22.5	1.5×10^4	0.64	0.42	1.4	<0.001	0.27	6.0	–	>5 hrs	–	–

† A = EMISSIONS FILTERED IN THE CHAMBER; (#) = MINUTES OF FILTRATION
F = EMISSIONS FILTERED AT THE TAILPIPE
D = DILUTION OF SYSTEM WITH ABSOLUTE FILTERED RURAL AIR; (#) = MINUTES OF DILUTION
C = CVS USED; # = CVS DILUTION SETTING
U = EMISSIONS INJECTED DIRECTLY INTO THE CHAMBER W/O FILTERING OR DILUTION
P = FRACTION OF DIESEL EMISSIONS INJECTED DIRECTLY INTO CHAMBER; (#) = PERCENT

†† UDC = URBAN DRIVING CYCLE
FET = FUEL ECONOMY TEST

* INSTRUMENT MALFUNCTION

** M = MERCEDES
Da = DATSUN
B = BUICK (GAS)

under various conditions (with irradiation, without irradiation, with primary particulates, without primary particulates, etc.). Hi-vol aerosol samples were collected following many of the experiments to determine the fate of the mutagenicity of the aerosols in the simulated environment.

In general, the irradiated systems were characterized by three distinct periods associated with the concentration of ozone: (1) low O_3 concentration; (2) rapid rate of increase of O_3 concentration; and, (3) slow decay of O_3 concentration. The period of maximum rate of change of the O_3 concentration was found to coincide with the maximum rate of production of aerosol (as determined by increased visibility degradation, increased rate of sulfate formation, decay of SO_2, NO_x, and reactive hydrocarbon, and formation of new particles). This conclusion is exemplified by the data of experiment #43 (see Figure 1).

Basically, two types of irradiated systems were studied with emphasis on aerosol formation and growth. The systems were segregated according to their photochemical reactivity or the rate of aerosol formation which corresponded well to the time required to produce the ozone peak following the initiation of irradiation (or the rate of ozone formation). In the more reactive systems, the ozone peak occurred 3 to 4 hours after the beginning of irradiation. The later experiments (#33-44 and #53-60) are indicative of the more reactive systems, the photochemical reactivity of the system being elevated by a high reactive hydrocarbon to oxides of nitrogen ratio (HC/NO_x). The less photochemically reactive systems were exemplified by the occurrence of an ozone peak in excess of 10 hours after the beginning of irradiation. This type of system necessitated long duration experiments (24 hour) in order to track the reactions past the ozone peak.

Data from one of the more reactive diesel emission/hydrocarbon systems are presented in Figure 1. The data include aerosol characterizations (top), gas concentrations (middle), and aerosol chemistry (bottom) throughout the six hour experiment. The peak or maximum ozone concentration for the system occurred about two hours after the beginning of irradiation. Corresponding to the formation of the ozone peak are an increasing visibility degradation (B_{scat}), a high rate of aerosol sulfate formation,

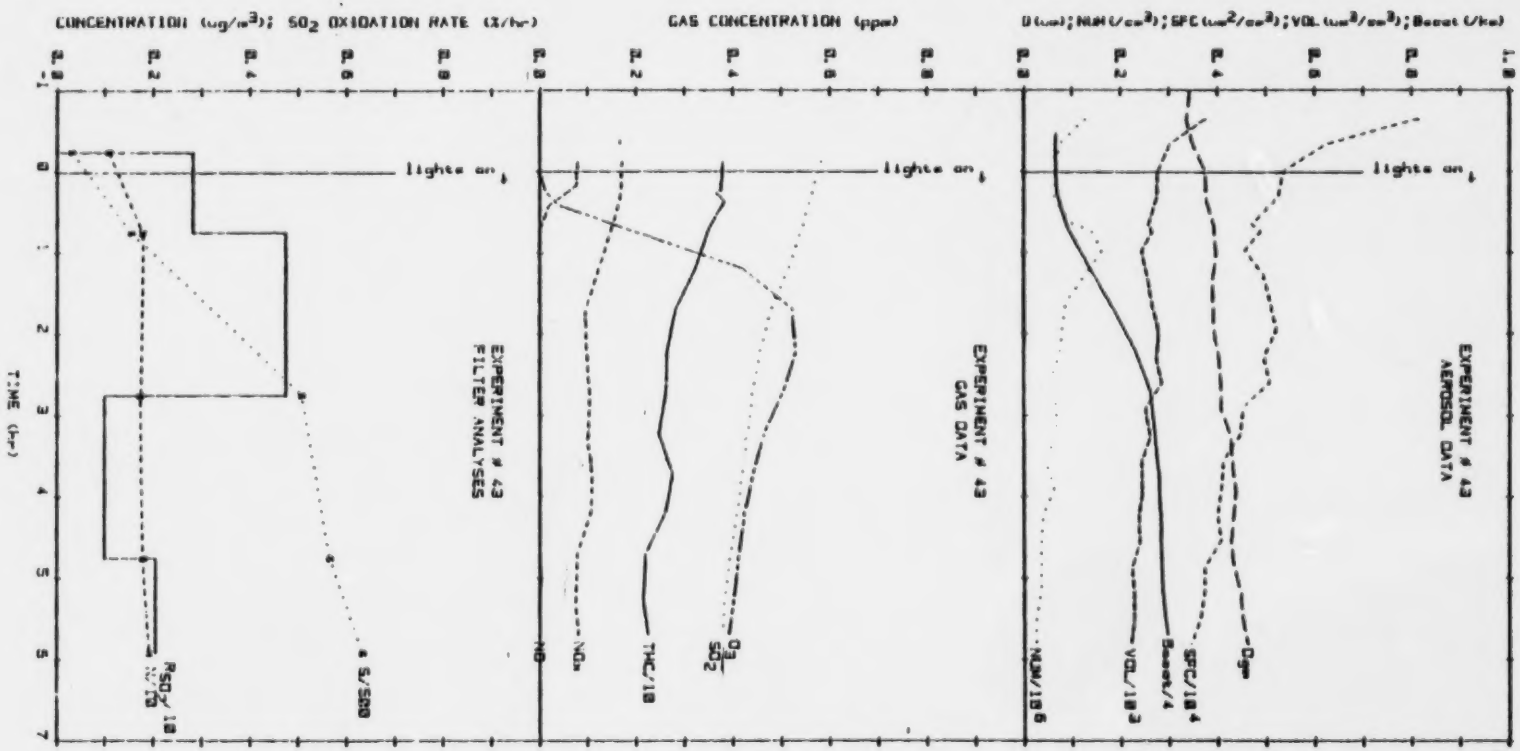

Figure 1. Aerosol, gas, and aerosol chemistry data for a diesel emission/hydrocarbon system exhibiting high photochemical reactivity.

maximum rates of decay of SO_2 and NO_x, and a significant but temporary increase in the concentration of the aerosol. With respect to aerosol formation and growth, the period of rapidly increasing ozone is the most active period for the system. Although carbon analysis of the aerosol was not available to determine the rate of production of organic aerosol for this particular experiment, data from other experiments indicated that the photochemical production of condensible sulfate was primarily responsible for the observed formation of new particles and growth of existing and new particles.* Aerosols collected at the completion of experiments of this type tended to exhibit less mutagenic activity than aerosols collected soon after introduction of diesel emissions into the chamber. This decrease in mutagenicity is attributed to the presence of ozone and is discussed in Section 6.

An example of one of the less reactive diesel emission/hydrocarbon systems is shown in Figure 2 (reactivity determined by propylene/NO_x ratio). In this particular experiment, the peak ozone concentration occurred about 19 hours after the beginning of irradiation. As in the case of the more reactive system, many of the important parameters of the experiment demonstrate the greatest change during the period when the ozone concentration is increasing most rapidly. In the less reactive system, the rate of sulfate formation is considerably less than in the more reactive system, but the total amount of sulfate formed is comparable (albeit in a much longer time).

A number of nonirradiated experiments involving diluted diesel emissions was performed to assess the importance of catalytic or heterogeneous reactions on aerosol formation and growth, to determine the rate of decay of aerosol and gas concentrations due to wall interactions, and to provide data on the effect of containment with time (aging) on the mutagenic

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*Experiment #59 revealed the potential importance of nitrates to form aerosols when sufficient ammonia was available to produce a nitrate compound (NH_4NO_3) which had a relatively stable solid phase (see Aerosol Nitrate).

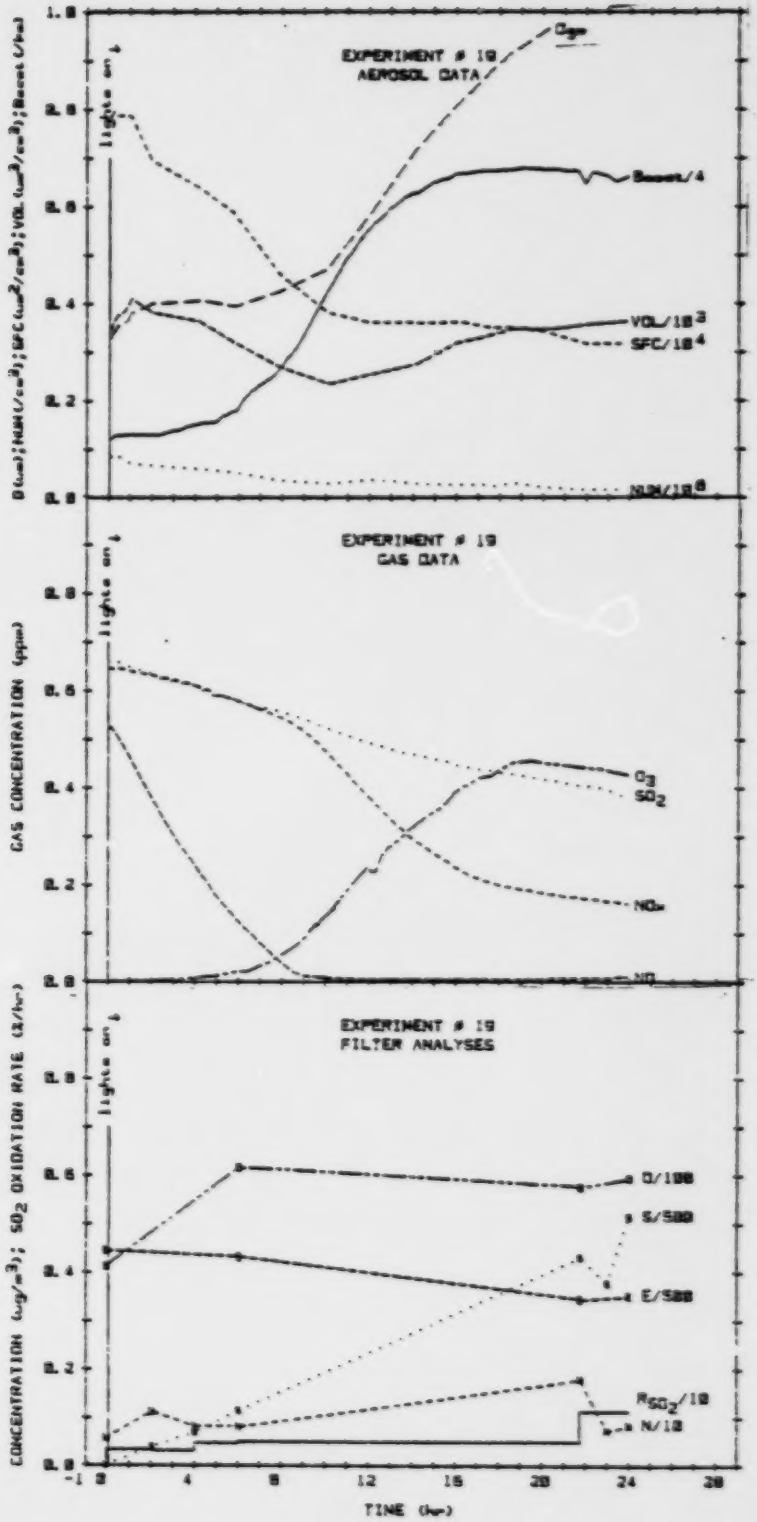

Figure 2. Aerosol, gas, and aerosol chemistry data for a diesel emission/hydrocarbon system exhibiting low photochemical reactivity.

activity of diesel emissions. One experiment was devoted to a measure of the rate of sulfate formation from the homogeneous reaction of SO_2 and ozone in a dark chamber. Results of these nonirradiated experiments typically indicate: (1) sulfate formation is very low ($R_{SO_2} < 0.2\%/hr$) for relative humidities less than 80% (experiments #3 and 32); (2) sulfate formation may become significant for relative humidities greater than 90% ($R_{SO_2} > 0.5\%/hr$ 94% RH) (experiment #35); (3) the simultaneous presence of a sub-ppm concentration of ozone and high relative humidity can produce rates of sulfate formation comparable to that of photochemical processes ($R_{SO_2} \simeq 1\%/hr$ at 94% RH and $O_3 \simeq 0.6$ ppm) (experiment #35); and, (4) the mutagenic activity of diesel emissions appears to increase with containment in a dark chamber (experiment #32).

Several basic irradiated $HC/NO_x/SO_2$ experiments were performed in which no diesel emissions were added to the system. The tests involved absolute-filtered rural air and sufficient quantities of HC (propylene), NO_x, and SO_2 to simulate the respective concentrations of gases contained in the diluted diesel emission/SO_2/HC systems. Such tests were designed to determine if the simple propylene/NO_x/SO_2 system was an acceptable surrogate for the more complex diluted diesel emission system and to establish baseline mutagenicity.

The irradiated $HC/NO_x/SO_2$ systems can be compared directly with diesel emission/SO_2/HC systems (with and without primary particulates) and diesel/gasoline-fueled auto emission/SO_2/HC systems (with and without primary particulates). A comparison of the former systems (experiment #29 versus 22 and 26) reveals a very similar reactivity (in particular, the peak ozone concentrations occur at a similar interval after the initiation of irradiation). This similarity indicates that the propylene added to the system is primarily responsible for the observed chemistry. Differences arise from a more rapid decay of O_3 after its peak in the $HC/NO_x/SO_2$ system and the influence of primary aerosol on B_{scat} and sulfate formation (see Primary Particulates). The diesel emission system without primary particulates also exhibits a larger B_{scat} than the $HC/NO_x/SO_2$ system.

The later series of experiments (#60 versus 57 and 58) display different photochemical reactivities. The production of ozone in the $HC/NO_x/SO_2$ system is much delayed when compared to the diesel exhaust systems. The delay in O_3 production indicates that HC species in the gasoline-fueled auto

emissions make significant contributions to the photochemical reactivity of the system (in contrast to the HC component of the diesel emissions). Consequently, the HC/NO_x/SO_2 system does not provide an accurate simulation of the diesel/gasoline-fueled auto emission/SO_2/HC system.

One experiment (#37) was performed with toluene, as opposed to propylene, as the reactive hydrocarbon. When compared with a similar experiment containing propylene (#43), the diesel emission/SO_2/toluene experiment exhibited lower rates of ozone and sulfate formation, but a larger B_{scat}. Chemical analyses of filter samples of experiment #37 did not account for the larger B_{scat} by increased organics. However, the geometric mass mean diameter of the aerosol was greater, indicating that the behavior may have been attributed to a more efficient aerosol size for light scattering.

In the subsections below, interpretations and discussions of specific features of the experimental observations (aerosol formation and growth, SO_2 oxidation, etc.) and influences of certain parameters (gas concentrations, primary particulates, relative humidity, etc.) are presented.

EXPERIMENTAL REPRODUCIBILITY

Prior to interpretation of the experimental data from the many distinct experiments demanded by the program scope, it was necessary to consider the uncertainty in experimental results due to lack of reproducibility. When considering the reproducibility of an experimental pair, we had to consider two different, though interrelated, aspects. The first was the degree to which the initial conditions (e.g., temperature, relative humidity, gas and aerosol concentrations, etc.) were reproduced. The second, and perhaps more significant aspect, was the degree to which the gas and aerosol reactions which took place during the experiment were reproduced. This latter comparison had to take into account differences which may have existed in the initial conditions. In the event of identical initial conditions, variations in the observed reaction rates may have been due to a compound which was present at undetectable concentrations, the outgassing of reactive species from the chamber walls during the experiment, the presence of interactive contaminants on the chamber surfaces, or fluctuations in light intensity due to changes in the line voltage.

To provide a measure of our ability to reproduce the gas and aerosol reactions of a given experiment, three experiments involving diluted diesel emissions were conducted as duplicates of previous tests. These three pairs were experiments 14 and 23, 16 and 24, and 19 and 22. These pairs represented low SO_2, high SO_2, and high hydrocarbon, respectively. The first two pairs were irradiated for six hours and used the CVS and absolute filtration system of the chamber. The last pair was irradiated for 24 hours and used only the chamber's dilution system. Hence, these experiments served to indicate the degree of experimental reproducibility under a number of different operating conditions.

The initial conditions for each of these experiments have been presented in Table 1, Log of Experiments. The experimental procedure and type and amount of hydrocarbons added were essentially exactly repeatable since these could be directly controlled. Prior to the introduction of diesel emissions, relative humidity was controlled by use of a water nebulizer and typically provided reproducibility to within a few percent.

Greater variations were found in parameters which were determined by the introduction of dilute diesel emissions into the chamber. These parameters included gas (in particular, NO and NO_2) and Aitken particle concentrations and visibility. In general, these parameters were not controlled individually but rather as a group by selection of the experimental procedure. As a result, the gas concentrations were generally reproducible to within $\sim$10%, and Aitken particle concentrations within $\sim$20%. Visibility being a function of not only aerosol concentration but also size, had a greater variance but was still reproducible to within a factor of two.

To investigate the reproducibility of the gas and aerosol reactions, the data from specific experiments presented in Appendix A must be compared. From the data, it appears that the parameter which is most difficult to reproduce is the rate of ozone formation. Ozone formation can be influenced by the NO, NO_2 and HC concentrations and light intensity. The first three of these can be difficult to simultaneously set at preselected levels. Hence, the differences of a factor of about 2.5 in the rate of ozone formation are not unreasonable. Additional discrepancies exist in the filter analyses data.

These, however, are believed to be primarily the result of relatively sparce data and, for nitrates, concentrations were close to the instrumental detection limits. For duplicate experiments, aerosol sulfate concentrations appear to be reproducible to within ~50%.

Taking the above aspects into account, the three pairs of duplicate experiments discussed earlier indicate a good degree of experimental reproducibility. For each pair, both the magnitudes and the rate of change of the measured parameters are in relatively close agreement as can be seen by side-by-side comparisons of the plots in Appendix A. These experiments also indicate that the chamber's filtering and dilution system, and the CVS used to dilute the auto exhaust may be operated reproducibly.

OXIDATION OF SO_2

Aerosol sulfate loadings as determined by IC and XRF analyses of periodic filter samples provided measures of the rate of sulfate formation which, when related to available SO_2, was expressed as the percentage of available SO_2 necessarily oxidized per unit time to produce the observed sulfate concentrations. These are the quoted values of SO_2 oxidation rates. All elemental sulfur indicated by XRF analysis was assumed to be in the form of sulfate.

The equation relating the rate of SO_2 oxidation, R_{SO_2}, to the concentration of available SO_2 and the rate of sulfate formation is

$$R_{SO_2} = \frac{2/3 \ \Delta \ SO_4}{(\text{available } SO_2)_{\text{available}}} \cdot \Delta t \qquad (1)$$

where ΔSO_4 is the increased concentration of aerosol sulfate ($\mu g/m^3$) formed in time Δt (hours) and $(\text{available } SO_2)_{\text{average}}$ is the average concentration of SO_2 ($\mu g/m^3$) during the interval Δt. The factor 2/3 is necessary to account for the increased molar weight of SO_4 over SO_2. An additional factor of 100 in equation 1 will result in units of % hr^{-1} for R_{SO_2}. As an example, assume that sulfate and SO_2 concentrations were observed to change from 10 and 1676 $\mu g/m^3$ to 95 and 1596 $\mu g/m^3$, respectively, in an 85 minute interval. The resulting rate of SO_2 oxidation would be 2.4% hr^{-1} (while the concentration of SO_2 decreased at a rate of 3.4% hr^{-1}). Daily calibrations of the Meloy

SO_2 Analyzer indicated that errors in the measurement of the concentration of SO_2 were negligible. Therefore, the principal uncertainty in determination of R_{SO_2} was due to the uncertainty in the measurement of the sulfate content of the aerosol. Analyses of duplicate and standard samples indicated that the uncertainty in the ion chromagraphic analysis for sulfate was typically less than 10%. Overall, the uncertainty in determinations of R_{SO_2} should also be less than 10%.

Gas data alone indicated losses of SO_2 as much as an order of magnitude greater than that necessary to account for the observed sulfate. Since this sulfur could not be accounted for in the aerosol phase, it is concluded that it was lost to the chamber walls. As a result, presented values of SO_2 oxidation rates (R_{SO_2}) use gas data only to provide the available SO_2 concentration at the time of the filter samples.

This program presented an opportunity to study the influence of a variety of parameters upon the oxidation of SO_2. For example, variations of relative humidity, reactive hydrocarbon concentration, SO_2 concentration, primary carbonaceous particulates, NO/NO_2 ratio, and irradiation were studied. While the survey type nature of the program did not allow quantification of the dependence of SO_2 oxidation on each of these parameters, some important trends were observed. These trends are summarized in Table 2. For example, an increase in the concentration of reactive hydrocarbon (HC) had a definite, positive impact on all of the listed variables. Except for a pronounced effect on B_{scat} (for RH > 90%)*, an increase in relative humidity had less dramatic effects. Increasing RH did indirectly result in less total sulfate formation (due to a significant reduction in available SO_2 through absorption by liquid water on the chamber surfaces) and appeared to increase the rate of SO_2 oxidation. Increasing RH had no apparent affect on the rate of ozone formation.

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* In some instances, the Meloy Sulfur Analyzer may not provide accurate measurements of the concentration of SO_2 at high RH. To minimize this error, the instrument used on this program was calibrated daily using a carrier gas having the same RH as that of the subsequent experiment.

TABLE 2. QUALITATIVE CORRELATIONS BETWEEN DEPENDENT AND INDEPENDENT VARIABLES

Independent Variable \ Dependent Variable	Sulfate Formation	B_{scat}	Rate of Ozone Formation	Rate of SO_2 Oxidation
HC Concentration	+	+	+	+
SO_2 Concentration	+	+	0	0
Primary Aerosol Concen.	+*	+	0	+*
RH	-	+	0	+

\+ Positive Correlation

\- Negative Correlation

0 No Correlation

* Trend indicated by data - not conclusive

Sulfate formation was found to be in approximate direct proportion to the concentration of both reactive hydrocarbons (propylene) and SO_2. The effects of increasing reactive hydrocarbon concentration was observed by comparing the results of experiments 17 and 25 and experiments 18 and 19. Such a comparison reveals that the reactive hydrocarbon is the driving force for the gas reactions (which result in gas-to-particle conversion). Differences in B_{scat}, sulfate formation, and the rate of SO_2 oxidation were all approximately proportional to differences in the reactive hydrocarbon concentration in the respective experiments. Ozone exhibited an even stronger dependence with a factor of about 5 increase in the rate of ozone formation for a doubling of the reactive hydrocarbon concentration. The results relating the rate of SO_2 oxidation to the concentration of the primary particulates of the diesel emissions and to relative humidity are unique, and are discussed in separate subsections which follow.

Two pairs of experiments (experiments #23-24 and 40-43) provided data on the effects of SO_2 concentration on sulfate formation. The data indicate that increasing the SO_2 concentration results in a direct increase in B_{scat} and the mass of sulfate formed. Although the rate of sulfate formation was approximately proportional to the SO_2 concentration, the rate of SO_2 oxidation did not appear to be affected (i.e., the rate of sulfate formation increased by essentially the same factor as the SO_2 concentration). B_{scat} increased by a factor of $\sim$2 for an order of magnitude increase in the SO_2 concentration.

PRIMARY AEROSOLS

Primary particulates of diesel emissions appear to have a positive influence upon the rate of formation of sulfate in an irradiated diesel emission/SO_2/HC system. Comparison of experiments #19 and 26, 43 and 38, and 57 and 58 (with and without diesel emission primary particulates, respectively) indicates a positive dependence of sulfate formation on the presence of primary particulates. At the end of six hours of irradiation, systems containing the diesel emission primary particulates had produced from 25 to 70 percent more sulfate than the respective system without the primary diesel emission particulates. As discussed above, the dependence of sulfate formation and reaction kinetics upon the initial conditions in the chamber placed an extreme burden on the resolution of variations (<50%) between experiments. While the weight of the data suggests a positive dependence of sulfate formation on the presence of primary particulates, data are not sufficient to unquestionably prove the dependence.

The carbonaceous nature of the primary particulates of the diesel emissions has been cited as a possible source for catalytic oxidation of SO_2 on aerosol surfaces in nonirradiated conditions (Novakov, 1973). During nonirradiated experiments at low relative humidities in our program, no significant sulfate formation was observed (experiments 3 and 32). A maximum rate of sulfate formation of less than 0.1%/hr existed under such conditions for primary particulate loadings well in excess of 1000 $\mu g/m^3$. Even this low rate of sulfate formation may have been due to a dark gaseous reaction in the chamber due to the presence of SO_2, NO_x, and low concentrations of reactive hydrocarbons in the diesel emissions.

At higher humidities, increasing amounts of sulfate were formed during nonirradiated tests of the diesel emission/SO_2 system (with primary particulates). In experiment #35 at a relative humidity of about 94%, an SO_2 oxidation rate of about 0.5%/hr was observed. This trend suggests significant quantities of sulfate may be produced at higher RH. (1% hr^{-1} is significant.) With the introduction of a sub-ppm concentration of O_3, this rate appeared to increase to about 1%/hr. However, the available SO_2 also dropped, due to absorption by liquid water on chamber surfaces, while the actual rate of sulfate formation remained about the same. Therefore, the apparent increase in SO_2 oxidation rate may be an artifact.

The role of the carbonaceous diesel emission primary particulates in promoting increased SO_2 oxidation and the process responsible for the increased sulfate formation at high relative humidities are uncertain. It is possible that the primary particulates served only as condensation sites for water vapor and did not directly participate in the subsequent heterogeneous reactions.

RELATIVE HUMIDITY

Conditions of high relative humidity may result in the presence of a significant liquid water content (LWC) of the aerosol due to condensation and/or the hygroscopic nature of the aerosol. While the presence of liquid water could certainly add to the mass of an aerosol, it might also serve as a medium in which dissolved SO_2 could be oxidized by heterogeneous reactions.

Irradiated tests involving high and low relative humidity are illustrated by experiments #41 and 43, respectively. The high humidity was apparently responsible for increased B_{scat}, SO_2 oxidation rate, aerosol mass, and aerosol nitrate. The reduced sulfate concentration during the high humidity test is attributed to the lower SO_2 concentration resulting from absorption of gaseous SO_2 by liquid water present on the chamber surfaces. This excessive decay in the concentration of SO_2 is much greater than is required to account for the observed sulfate formation.

O_3/SO_2 REACTION

One nonirradiated experiment (#54) was devoted to a measure of the rate of the reaction of O_3 and SO_2 in the chamber. Since losses of either of the gases to the chamber walls would influence the apparent rate of the reaction, determinations of the reaction rate were made from observations of aerosol sulfate formed by the reaction. Concentrations of O_3 and SO_2 similar to those of many of the irradiated experiments were added to the chamber. Subsequent lo-vol aerosol samples obtained at regular intervals provided the necessary aerosol sulfate concentrations.

The results of the experiment indicate a rate for the O_3-SO_2 reaction of $\simeq 1.75 \times 10^{-20}$ cm^3/molecule-sec or the oxidation of SO_2 at a rate of about 0.1%/hr to produce the observed aerosol sulfate. This is in contrast to the rate set by Davis (1974) of $<10^{-22}$ cm^3/molecule-sec. However, even at the higher rate observed in our chamber, the O_3-SO_2 reaction is not likely to be significant in the atmospheric conversion of gaseous SO_2 to aerosol sulfate, since other reaction rates (both homogeneous and heterogeneous) may be an order of magnitude larger.

NITRATE AEROSOLS

As a rule, no significant levels of aerosol nitrate were observed in these experiments. Typical measured levels of aerosol nitrate as determined by ion chromatographic analysis of filter samples were about 1 $\mu g/m^3$, approximately the blank level of the filter. With the addition of ozone into the diesel emission/hydrocarbon system (e.g., see experiment #33), the concentration of aerosol nitrate appeared to increase temporarily. With the addition of ozone at high humidity (see experiment #35), significant aerosol nitrate was formed and persisted. Using an impinger sampler containing a dilute aqueous solution of boric acid, ammonia concentrations for all tests (except experiment #59 where ammonia was deliberately introduced into the system) were less than 10 ppb.

In one experiment (#59), 10 ppm of ammonia was introduced into the chamber prior to irradiation. Contrary to the results of similar experiments not containing significant concentrations of ammonia, increasing and substantial concentrations of aerosol nitrate were observed on filter samples.

The final sample collected at the end of the six hour irradiation period revealed an aerosol nitrate concentration in excess of 1000 $\mu g/m^3$; about three times as large as the measured sulfate concentration. In this experiment, there was very good agreement between the measured concentration of aerosol nitrate and the observed decrease in NO_x (assuming that NO_2 was oxidized to form nitric acid).

While these data are certainly limited in quantity, we do not doubt that the presence of ammonia is responsible for the formation of substantial aerosol nitrate. From the available data, we are not able to determine if the presence of ammonia was responsible for increased production of gaseous nitrates (either by increasing the rate of NO_x oxidation or by undergoing oxidation itself) and/or was responsible for aerosolizing those nitrates that were ordinarily present as vapors in all of the irradiated experiments. However, the facts that the rate of NO_x decay was not accelerated and that the aerosol nitrate can be accounted for by the observed loss of NO_x appear to point to the latter hypothesis. This conjecture is further developed below.

The vapor pressure of nitric acid (assumed to be the predominant product of NO_2 oxidation) is sufficiently high that nitric acid aerosols are not likely. The interaction of ammonia and nitric acid produces ammonium nitrate which can be found in the aerosol phase. Stelson et al (1979) indicate that the equilibrium concentration of aerosolized ammonium nitrate, which also may sublime, is dependent upon the concentration of available ammonia and nitric acid. Thus, while there may have been an abundance of gaseous nitric acid in many of the irradiated experiments, sufficient concentrations of ammonia were not present to result in significant equilibrium concentrations of aerosol ammonium nitrate.* It follows that the introduction of ammonia to the system in experiment #59 allowed the majority of the available nitric acid to be aerosolized in the form of ammonium nitrate. The possible effects of ammonia upon the aerosol sulfate concentration did not appear significant; however, the presence of NH_3 may have affected the overall photochemistry of the system as the ozone peak

*We observed ammonium nitrate to be the primary constituent of fog water during a study at Travis Air Force Base (near Sacramento) in January-February, 1973 (Mack et al, 1973).

did not occur during the six-hour experiment. The O_3-NH_3 reaction (Olszyna and Heicklen, 1972) could account for the depression of the O_3 concentration as well as some of the aerosol nitrate.

CARBON AEROSOLS

In many experiments, lo-vol filter samples were obtained and analyzed for elemental and organic carbon. The carbon analysis (Johnson et al, 1979) consisted of a pyrolytic separation of the organic and elemental components followed by conversion to CH_4 and analysis by flame ionization. These analyses indicated that the initial diesel emission aerosol contained elemental carbon and various condensible organic compounds in a ratio of about 5 to 1, respectively.

As a consequence of the pyrolytic separation of organic and elemental carbon in the analytical procedure, it was possible that a portion of the organics were pyrolyzed to form what would have appeared to be elemental carbon. This process is believed responsible for the few instances of increasing elemental carbon concentration presented in Appendix A. In consideration of the potential for the formation of artifact elemental carbon, the results are best viewed as upper limits for elemental carbon and lower limits for organic carbon.

During the chamber experiments, the concentration of elemental carbon decreased (as expected) as a result of the loss of particles to the chamber surfaces by a combination of diffusion and sedimentation. On the other hand, organic carbon, which should have suffered losses at a rate proportional to that of the elemental carbon, exhibited a slower net loss or even a potential net increase during the irradiated experiments as condensible organic vapors were formed through photochemical processes. This contrasting behavior of the elemental and organic components of aerosol carbon was clearly indicated in experiment #18. Even with the increases in organic and losses in elemental carbon, the concentration of elemental carbon remained significantly greater than that of organic carbon due to the initial concentration imbalance.

Significant increases in the organic component of the aerosol were observed in a number of experiments (e.g., experiments #18, 19, 25, 26, 28 and

29). Comparison of experiments #19 (with primary particulates) and #26 (without primary particulates) suggests that the presence of the primary particulates inhibited the formation of organic aerosol. However, in the presence of diesel emission primary particulates which contained a large quantity of organics, the ability to resolve additional organic material formed by photochemical processes may have been hampered.

DISCUSSION

The low HC/NO_x ratio contained in diesel emissions was not effective in initiating photochemistry. Propylene/NO_x/SO_2 systems exhibited photochemical reactivities (in terms of NO decay, O_3 formation, etc) similar to diesel emission/SO_2/propylene systems. Systems composed of diesel/gasoline-fueled engine emissions/SO_2/propylene displayed photochemical reactivities distinct from those of comparable propylene/NO_x/SO_2 systems, indicating that the hydrocarbon components of the gasoline-fueled engine emissions represented a significant contribution to the system.

While the diesel emission primary particulates appeared to have a negligible effect upon the photochemical reactivity of a system, they did appear to result in an increase in the total sulfate produced. There is also some indication that the presence of the primary particulates may have inhibited the formation of organic aerosol. SO_2 oxidation rates in nonirradiated tests were significant (>0.1%/hr) only in cases of high relative humidity. The simultaneous presence of high relative humidity and O_3 under nonirradiated conditions appeared to have been responsible for SO_2 oxidation in excess of 1%/hr. At low relative humidities, sulfate formation due to the O_3/SO_2 reaction resulted in the oxidation of SO_2 at the rate of about 0.1%/hr.

No significant concentrations of aerosol nitrate were formed in irradiated tests under conditions of very low NH_3 concentrations (<10 ppb). In a single experiment in which 10 ppm of NH_3 was introduced into the chamber, a substantial amount of nitrate aerosol was observed. This occurrence of aerosol nitrate was attributed to the reaction of available gaseous nitric acid with the NH_3 to produce a nitrate compound with a reduced vapor pressure (NH_4NO_3).

Section 5
AEROSOL FORMATION AND GROWTH

The presence of significant quantities of diesel emissions in an urban environment may affect aerosol formation and growth not only through potential modifications of the photochemistry, but also through physical processes. The primary particulates of diesel emissions represent condensation sites for the condensible vapors formed by gas-to-particle conversion. Consequently, new particle formation may be inhibited as this condensible material is primarily consumed by the growth of existing particles as the formation of mass continues. Diesel emissions may contribute to a significant modification of the size distribution and mass loading of urban aerosols.

As noted in the earlier discussions, the maximum rate of change in aerosol mass was associated with the formation of the ozone peak in the irradiated experiments (or to the period immediately subsequent to the depletion of NO). The most significant fraction of the aerosol growth was attributed to the production of sulfates (except in experiment #59 where a large concentration of aerosol nitrate was formed due to the addition of NH_3).

SECONDARY AEROSOL FORMATION

The formation of new aerosol particles was dependent upon two parameters: (1) the availability of condensation nuclei to relieve the saturation of condensible vapors prior to new particle formation; and, (2) the rate at which condensible vapors were being produced. It is apparent that the effects of the two parameters are not independent; that is, for a given aerosol concentration, the probability of new particle formation is dependent upon the rate of production of condensible vapors (and vice versa). The abundance of primary particulates in the diesel emissions provided an excellent source of condensation nuclei for condensible vapors formed by photochemical reactions.

There were two distinct periods in these experiments where new particle formation was common: (1) soon after the initiation of irradiation, and (2) in association with the formation of the ozone peak (and the maximum rate of sulfate formation). Although the rate of production of condensible vapors was (in many cases) not a maximum during the early stage of the experiments (first 15 minutes), frequently (see experimental data in Appendix A) there was an insufficient concentration of condensation nuclei to prevent the formation of new particles. The data presented in Appendix A relied upon aerosol characterizations as determined by the electrical aerosol analyzer (EAA) and Royco optical particle counter. Since the realistic lower limit of particle resolution offered by this capability was about 0.01 μm diameter, the formation of new particles was not immediately detected. Particularly in the case of experiments where the primary particulates of the system had been removed by filtration, the maximum concentration of particles formed (as determined by the EAA) may have been low by at least an order of magnitude as compared to the number determined by an Aitken nuclei counter.

The formation of new particles immediately subsequent to the initiation of irradiation was soon followed by a decay of the aerosol concentration due to coagulation. This concentration decay was due to the high mobility of the tiny new particles which resulted in a high probability of their collision with other aerosols. The particle concentration soon achieved a sufficient value to adsorb new condensible vapors and capture any new particles prior to their growth to an observable size.

The second period of particle formation in irradiated experiments was associated with the formation of the ozone peak. This period, during which ozone was being produced at its most rapid rate, was responsible for the highest rate of sulfate formation. In many cases, the increase in the rate of sulfate formation was sufficient to disrupt the equilibrium between aerosol concentration and rate of production of condensible vapors established in the early part of the experiment. The result was the formation of new particles during a period of the experiment several hours after the initiation of irradiation. As in the earlier period of aerosol formation, the increase in particle concentration was followed by a decrease (due to condensation and coagulation) to a new equilibrium aerosol concentration.

Empirically, after an irradiated system had reached a particle concentration equilibrium, new particle formation was found to occur for rates of ozone formation in excess of 0.1 ppm/hr and an SO_2 concentration greater than about 0.1 ppm. Both of these conditions were required, with a high rate of ozone formation or a high concentration of SO_2, only, not being sufficient to result in new particle formation. Examples of the formation of new particles during the intermediate period of an experiment may be found in many of the experiments (e.g., #18, 21, 22, 24, 25, 26, etc.).

A detailed discussion of the processes controlling new particle formation in the presence of primary particulates has been presented by McMurry et al (1979). The authors suggest that an indicator for new particle formation may be a dimensionless parameter, L, which is dependent upon available aerosol surface area and the rate of formation of condensible molecules, as well as properties of the condensible molecules. They propose that for $L < 0.1$, new particle formation will dominate; while for $L > 0.1$, condensation on available aerosols will be sufficient to prevent new particle formation. Using the same assumption as McMurry et al (1979) (i.e., that sulfates represented the major condensible products of the irradiated SO_2/NO_x/propylene system), we calculated L for several experiments involving either new particle formation or no new particle formation. In contrast to McMurry et al (1979) who used the decay of SO_2 as the rate of formation of condensible molecules, we used measured values of aerosol sulfate to determine the rate of formation of condensible molecules.* Where there was new particle formation, values of aerosol surface area and the rate of sulfate formation were selected just prior to that period. The values of our calculated L's demonstrated little correlation to the observed new particle

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* In the Calspan chamber, which has a low surface-to-volume ratio ($\sim 0.2\ m^{-1}$) and inert walls, the concentration of SO_2 was observed to decay as much as an order of magnitude faster than necessary to account for the measured formation rate of aerosol sulfate (see Oxidation of SO_2).

formation. New particle formation was observed for values of L as large as 22.5 (experiment #18) and as low as 0.24 (experiment #25).* Likewise, no new particle formation was observed for the L as high as 9.58 (experiment #16) and as low as 0.48 (experiment #36). For the range of experimental conditions of this program, the value of L does not provide a meaningful indication of the probability of secondary aerosol formation.

AEROSOL GROWTH

As expected, the period of maximum particle growth (maximum rate of condensation of condensible vapors) was associated, in many cases, with the production or generation of new particles. While some of the observed aerosol growth was attributed to organics, most of the growth was due to the formation of aerosol sulfate. Good agreement between sulfur determinations by x-ray fluorescence (total sulfur) and ion chromatography (soluble sulfate) indicated that only an insignificant portion of the aerosol sulfur could have been associated with organic compounds.

In the data presented in Appendix A, aerosol growth is most directly represented by increases in the geometric mass mean diameter, Dgm. Determinations of Dgm assumed a log-normal aerosol distribution and were analogous to the determinations of mass mean diameter for a normal particle distribution. The value of Dgm was influenced by new particle formation, particle coagulation, and the growth of the aerosol by the condensation of vapors (primarily sulfates). The formation of new particles with diameters much less than those of the existing aerosol caused the value of Dgm to decrease (e.g., experiments #12, 25 and 38) while coagulation immediately following new particle formation (e.g., experiment #38) and general particle growth by condensation of vapors onto existing particles (e.g., experiment #16 and 19) resulted in an increased Dgm.

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* Due to the typically large primary aerosol loadings of the diluted diesel emission system, the regime L < 0.1 was never observed.

Aerosol data from irradiated diesel emission/SO_2/HC systems with (experiment #19) and without (experiment #26) diesel primary particulates are displayed in Figure 3. As indicated, the presence of diesel primary particulates apparently curtails new particle formation by providing condensation sites for condensible products of the reactions. The resulting growth of existing particles produces a larger D_{gm} (geometric mass mean diameter) and fewer total particles than the similar primary particle-free system. These larger particles are in the size range which is more likely to be retained deep within the human respiratory system.

Visibility degradation data indicated by the B_{scat} curves of Figure 3 exhibit a trend common to many of our tested HC + NO_x + SO_2 systems; that is, B_{scat} tracks very closely with the concentration of ozone and also tracks D_{gm}. After irradiation and O_3 formation, B_{scat} is greater in the system containing the diesel primary particulates than in the system without the primary paeticulates, even though the particle concentration (NUM) is less in the former. This larger B_{scat} of the system containing the primary particulates is attributed to the larger mean particle size (more efficient light scatterer). It is interesting to note that the difference in final B_{scat} values between the two systems is approximately the B_{scat} value of the primary particulates. This correlation is apparently fortuitous.

For typical irradiated, diluted diesel emission systems, Dgm began in the range of 0.2 to 0.4 μm and increased during the experiment to about 0.5 μm. The growth of aerosols for three separate experiments is presented in Figures 4, 5 and 6. The data in each figure is presented as the volume change per change in the log (base 10) of particle diameter versus particle diameter for several pertinent times within the experiment.* With this presentation, the integral of the area beneath each curve represents the aerosol volume at that given time. As expected, this presentation confirms the shift in mean aerosol volume to larger particle diameters as aerosol growth continued.

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* The unusual bulge in data for particle diameter >1 μm is due to the merging of EAA data (based on charged particle mobility) and Royco data (based on particle light scattering characteristics). The discontinuity in the data at the point the two data sets meet is attributed to two factors: (1) at the extremes of their ranges, both instruments display high uncertainty; and (2) the instruments are based on distinctly different particle characterization processes.

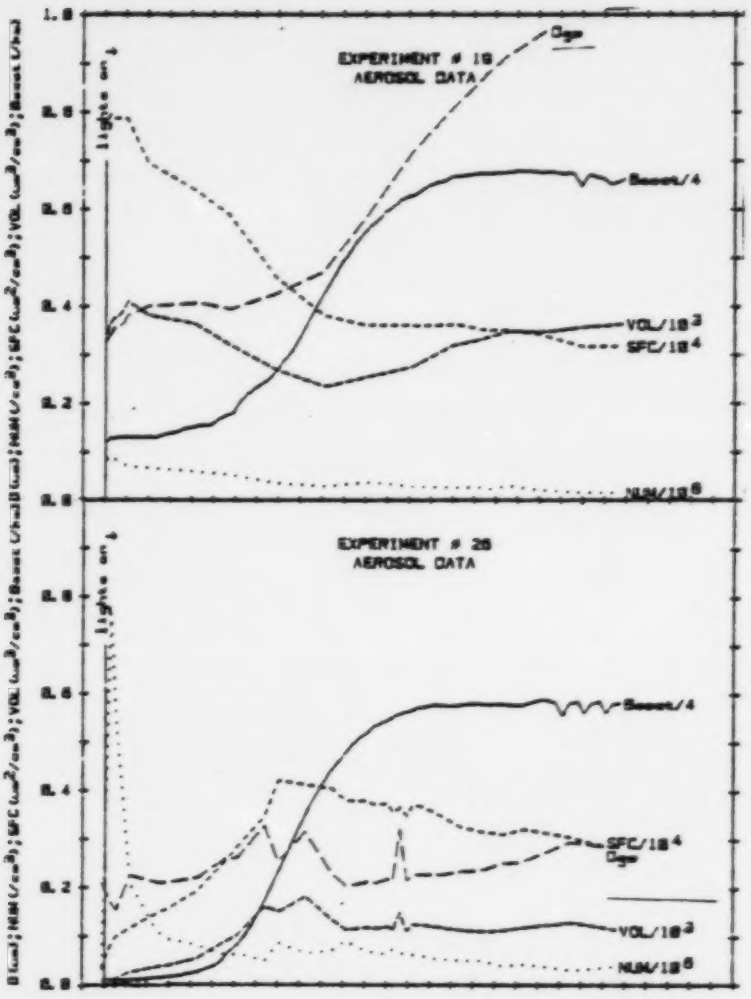

Figure 3. Aerosol and B_{scat} data from irradiated diesel emission/SO_2/HC systems with (upper) and without (lower) diesel primary particulates.

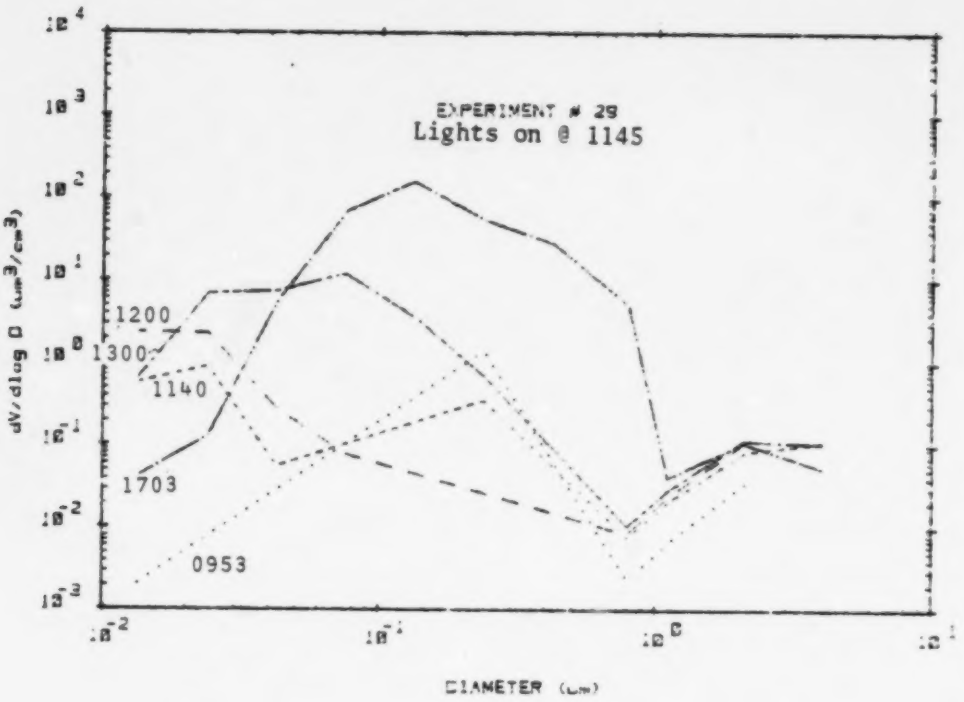

Figure 4. Evolution of aerosol size distribution for an irradiated $HC/NO_x/SO_2$ system without primary particulates.

Aerosol growth for a simple $HC/NO_x/SO_2$ system with only a few primary aerosols (Experiment #29) is presented in Figure 4. The five particle distributions shown exhibit the primary particle distribution (0953), effects of dark chamber (1140), and the aerosol evolution after the initiation of irradiation (1200, 1300 and 1703). While the dark reaction prior to the initiation of irradiation did result in the formation of new particles, the mass (volume) of these secondary particles was small. With the initiation of irradiation, the aerosol mass began to increase significantly, along with an increase in the mass mean diameter, principally due to increased sulfate from the SO_2 - OH reaction.

Aerosol formation and growth in a diesel emission/SO_2/HC system with a low concentration of primary particulates (Figure 5) undergoes changes very similar to those of the simple $HC/NO_x/SO_2$ system. Soon after the beginning of irradiation, new particles are formed at the low end of the size spectrum. These particles and the small concentration of primary particulates grow and/

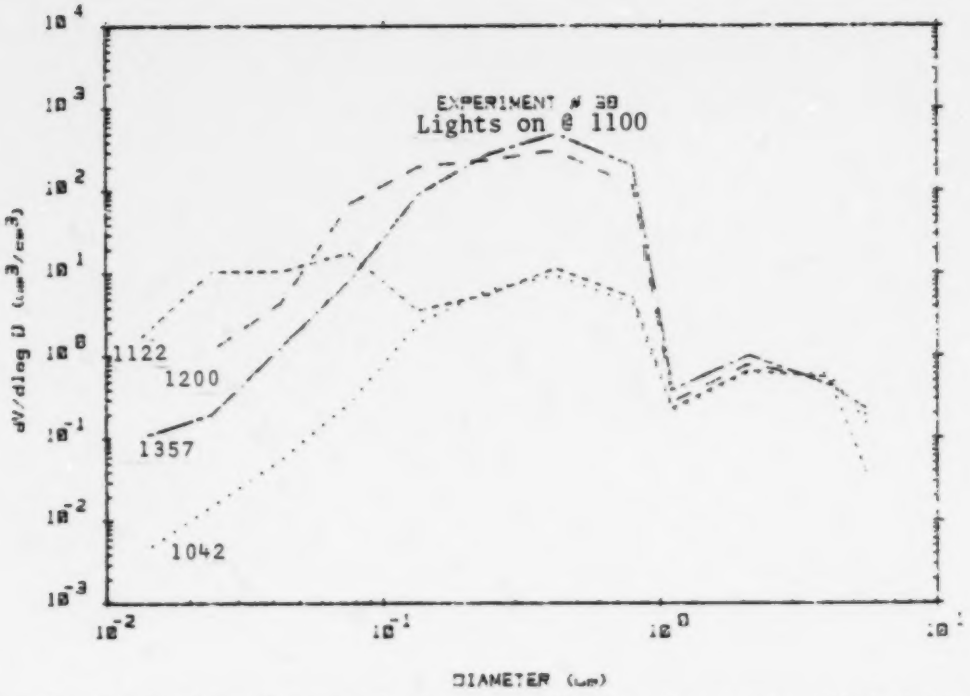

Figure 5. Evolution of aerosol size distribution for an irradiated diesel emission/SO_2/HC system with low concentration of primary particulates.

or coagulate, resulting in the observed increase in mass mean diamter and an eventual equilibrium of the concentration of particulates. Close examination of Figure 5 reveals that the aerosol distribution is weighted more towards larger particle sizes than the distribution in Figure 4 at comparable time intervals after the initiation of irradiation. That is, the irradiated diesel emission/SO_2/HC system exhibits a larger mean aerosol size than the irradiated HC/NO_x/SO_2 system. This feature of the data is likely the result of different initial conditions of the experiments; in particular, the concentration of primary particulates and the HC/NO_x ratio.

In contrast, a typical evolution of the aerosol size distribution of an irradiated diesel emission/SO_2/HC system with a large concentration of primary particulates of the diesel emissions is presented in Figure 6. While there was some new particle formation soon after irradiation began (1013), for the most part, aerosol dynamics were dominated by growth of primary

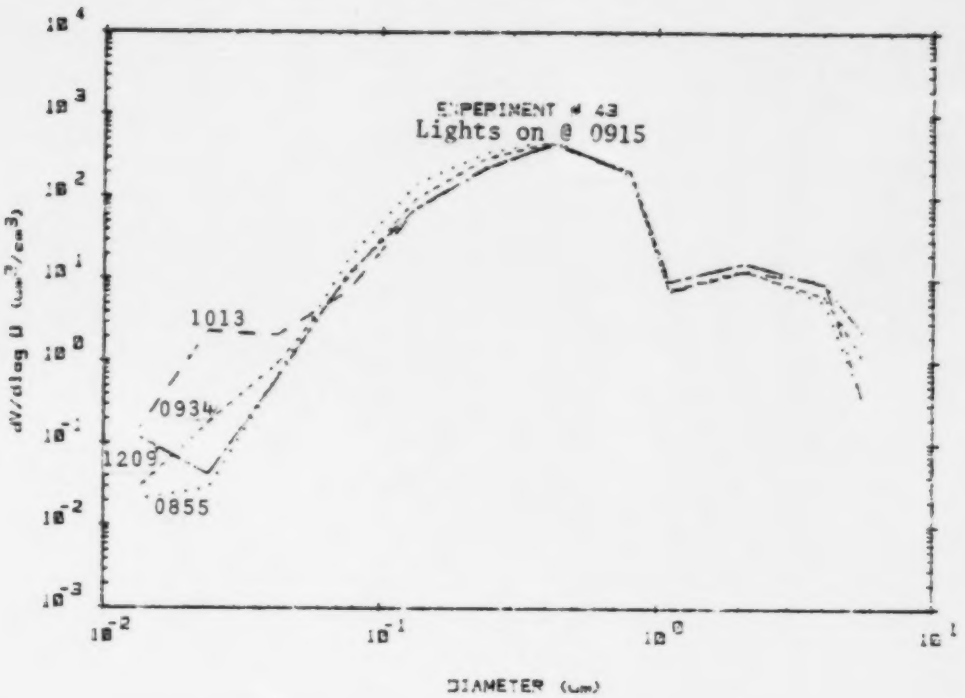

Figure 6. Evolution of aerosol size distribution for an irradiated diesel emission/SO_2/HC system with a large concentration of primary particulates.

particulates. As shown in Appendix A, this growth of aerosol increased the geometric mass mean diameter by about 25% (from ∿0.38 μm to ∿0.48 μm) during the six hour experiment. This change in the aerosol size distribution is significant, but not nearly so dramatic as the evolution of the aerosol size distribution in a system containing a low concentration of primary particulates. Although the aerosol exhibited in Figure 6 contained slightly more mass than that presented in Figure 5 (see Appendix B, Table 4), the primary difference in the two aerosols was the distribution of mass according to size.

AEROSOL SURFACE AREA

Aerosol samples of diesel particulates obtained both at the exhaust of the auto (at the high exhaust temperatures) and directly after injection into the chamber have been analyzed for available surface area by the BET

(multi-point) method (using a mixture of helium and nitrogen gases). Aerosols sampled at the exhaust exhibited surface areas of about 140 m^2/gm with excellent repeatability. Surface areas of about 70 m^2/gm were measured for aerosols sampled from the chamber after about 30 minute aging with no exposure to irradiation. The analysis of the latter sample exhibited poor repeatability with an actual range of data from 37 to 150 m^2/gm.

At this time, the difference in the available surface area of the two sample types is attributed to the high temperature of the aerosol sample at the auto exhaust. It is suspected that some higher molecular weight organics in the diesel exhaust would not condense onto the primary particulates at the elevated temperatures. As the sample was injected into the chamber and allowed to cool, the remainder of the condensible vapors of the diesel exhaust was adsorbed by the primary particulates. Hence, the available surface area of the aerosol was reduced. The non-repeatability of the latter samples may have been due to the volatility of the condensed vapors on the primary aerosol.

Aerosol samples of diluted diesel emissions collected with an electrostatic precipitator were observed by scanning electron microscopy. The resulting micrographs revealed aerosol particles which were typical of diesel soot. Individual particles (generally with diameters less than 1 μm) consisted of aggregates of tiny spherical particles assembled in a chain-like fashion. A portion of the aggregations could have been artifacts, formed during their collection by electrostatic precipitation. Individual spheres of these chain aggregates exhibited diameters of about 0.05 μm. In some cases, an amorphous substance appeared to coat the aggregates.

DISCUSSION

Aerosol formation and growth in systems not containing primary particulates follow similar qualitative trends in irradiated HC/NO_x/SO_2 and diesel emission/SO_2/HC systems. The presence of primary particulates of the diesel emissions results in a reduction of the number of secondary aerosols formed, larger mean particle sizes, and increased visibility degradation. The increased mean particle size means that a larger fraction of aerosol will be contained in the 0.5 to 3 μm diameter range, which is known to be retained deep in the lungs. This could represent an increased health hazard since mutagenic compounds are known to be associated with diesel particulates.

Irradiated systems containing the primary diesel exhaust aerosol contained consistently larger aerosol mass loadings than comparable systems not containing the primary diesel aerosol. In addition to the contribution to mass loading by the primary aerosol, an increase in aerosol mass was associated with the additional sulfate produced in the presence of the primary diesel aerosol. Based upon aerosol analyzer data, the increased aerosol mass loading ranged from less than 10 percent (experiments #43 and 38) to almost 300 percent (experiments #19 and 26).

Section 6
MUTAGENIC RESULTS

Diesel emissions contain significant concentrations of known and suspected mutagenic compounds which are associated with the diesel primary particulates (National Academy of Sciences, 1972). With continued escalation in the fraction of total auto emissions comprised of diesel emissions, it is important that the potential health effects related to the mutagenic activity of diesel emissions be studied. For such a study to be valuable, information must be available on the influence of the exposure of diesel emissions to the atmosphere upon their mutagenic activity. In the atmosphere, the mutagenicity of diesel emissions might be modified by: (1) reactions among various constituents of the diesel emissions following dilution; (2) photolysis of mutagenic compounds; and, (3) reaction with atmospheric gases and aerosols, principally NO, NO_2, O_3, OH or RO_2.

One task of the Calspan smog chamber program was to provide preliminary experimental data correlating the mutagenic activity of diesel emissions to the duration of exposure to simulated urban atmospheres. The diesel emissions, generated in the experiments described in Section 4, were exposed to a variety of conditions including: dilution followed by containment (nonirradiated); dilution followed by irradiation; dilution, the addition of SO_2 and reactive hydrocarbons, and irradiation; and dilution followed by containment in the presence of a sub-ppm concentration of ozone with no irradiation. The experiments also provided data on the mutagenic activity of photochemical aerosols produced by irradiation of primary particle-free diesel emission/SO_2/hydrocarbon and HC/SO_2/NO_x systems.

Of particular value to the program was the ability to obtain a sufficient quantity of aerosol from the subject systems to allow a complete mutagenic analysis by the Ames test. The large volume of the Calspan chamber

(600 m^3) containing a realistic aerosol mass burden (e.g., 100 $\mu g/m^3$) provided an adequate source of aerosol. In order to obtain aerosol samples from a large fraction of the chamber air in a reasonable period of time, a system of three hi-vol samplers was installed in the chamber. The system was recirculatory in nature, exhausting the filtered air back into the chamber. This method provided a closed filtration system minimizing the possibility of contamination. Approximately 60% of the chamber aerosol could be filtered in three hours of sampling, providing a sample mass on the order of 0.1 gm. The samples were collected upon 8 x 10 inch glass fiber filters (Pallflex T60A20). For the latter series of tests (experiments 31-60), the filter samples were wrapped in aluminum foil, previously cleaned with methylene chloride, to prevent possible reactions involving the organic carbons. All samples were shipped to EPA's Health Effects Research Laboratory for mutagenic testing by the standard Ames test.

Hi-vol aerosol samples, usually containing fractions of a gram quantities of primary and secondary aerosols, were collected and submitted to the Health Effects Research Laboratory of EPA (Research Triangle Park, North Carolina) for mutagenic analysis by the Ames bioassay test. A sample extract (methylene chloride solvent) was subjected to the Ames test. Several strains of bacteria were used in the bioassay, allowing the test to be specifically sensitive to a variety of types of mutagens.

The results of the mutagenic tests for the indicated experiments are presented in Table 3. The table includes an experiment title, a designation of irradiated (I) or nonirradiated (dk) conditions, the time interval (age in hours) between the introduction of the diesel aerosol into the chamber and the initiation of the hi-vol sampling, the response of specific bacteria to the residue of the sample extract (100 µg quantity) with (+) and without (-) mammalian activation, and the relative level of the observed mutagenicity of the sample as compared to other samples of that particular data set. For each strain of bacteria, the results are given as the response (number of revertant cultures) per 100 micrograms of extract of the aerosol sample. The larger the response (i.e., more revertant bacterial cultures), the higher the mutagenic activity of the sample.

The mutagenic analyses of the hi-vol aerosol samples were performed in the sets indicated in Table 3. To offer maximum confidence in the interpretation of these results, we prefer to compare results from those experiments within a particular set. In further qualifying the following interpretation, the quantity of tests was not sufficient to provide a quantitative interpretation, and there were few duplicate experiments with which the repeatability of the tests can be determined.

In experiment sets 1 and 3 of Table 3, data indicate that the mutagenic activity of the diesel emissions increased with containment in a nonirradiated chamber. Comparison of experiments 1 (background) and 3 (aged) shows that diesel emissions aged for different intervals in two separate experiments exhibited an increase in mutagenicity with age. In order to ascertain that the observed change in mutagenicity was not due to variations in the primary diesel emissions between experiments, a subsequent experiment was performed in which two hi-vol aerosol samples were obtained from a single dilute diesel emission system. The first hi-vol sample (32-1, background) was obtained within the one-hour period immediately after introduction of the diesel emissions into the chamber and the second (32-2) was obtained in the 2.5 hour period following about 5.5 hours of containment in the nonirradiated chamber. This experiment (#32) also indicated an increase of mutagenicity of the dilute diesel emissions with the length of containment in the nonirradiated chamber.

A similar series of tests for dilute diesel emissions exposed to irradiation (experiments #2 compared to #1 background, and #44) also exhibited a slight increase (experiment #44) or little variation (experiment #2) in mutagenicity with length of exposure. These data suggest that irradiation per se was not effective at breaking down those compounds associated with the diesel aerosol which contributed to the observed mutagenicity.

Dilute diesel emission systems containing sufficient quantities of reactive hydrocarbon to result in ozone formation exhibited decreases in mutagenicity when exposed to irradiation (i.e., experiment sets 2 and 3). Products of the photochemistry included sulfate and condensible organic aerosols, nitrate vapors, ozone, and highly reactive free radicals (see Section 4). A subsequent experiment in which a sub-ppm concentration of

Table 3
RESULTS OF MUTAGENIC ANALYSES

AUTO	EXPERIMENT			AGE (hrs)	SPECIFIC ACTIVITY (100 μg)/SLOPE (revertants/μg) TA 1535 –	TA 1535 +	TA 1537 –	TA 1537 +	TA 1538 –	TA 1538 +	TA 98 –	TA 98 +	TA 100 –	TA 100 +	CHANGE†
MERCEDES	**URBAN DRIVING CYCLE**														
	1. Mut. Bkgd.	SET 1	dk*	0.5	NEG**	NEG	47.3 (0.27)	47.3 (0.34)	91.3 (0.72)	114.0 (0.97)	322.8 (2.36)	218.6 (1.22)	528.8 (2.77)	386.4 (2.51)	0
	2. Irrad. Mut.		I	6.0	–	–	36.8 (0.20)	38.3 (0.28)	66.3 (0.51)	90.5 (0.76)	308.5 (2.26)	160.9 (0.96)	639.8 (4.94)	388.4 (2.41)	0
	3. Aged Mut.		dk	6.0	NEG	NEG	215.9 (2.02)	186.4 (1.94)	201.7 (1.88)	378.7 (3.37)	1307.1 (11.9)	614.4 (4.83)	–	1016.3 (8.32)	++
	4. Irrad. Mut. (Add HC)		I	6.0	NEG	NEG	136.4 (1.29)	119.8 –	281.5 (2.63)	299.3 (2.76)	753.1 (6.51)	482.1 (3.70)	–	650.3 (6.52)	+
	FUEL ECONOMY TEST CYCLE														
	12. w/o Prim. Part.		I	6.0	–	–	–	–	–	–	280.6 (2.40)	188.8 (1.43)	–	–	—
	13. Mut Bkgd.		dk	0.5	–	–	313.9 (2.98)	282.2 (2.99)	403.5 (3.90)	479.2 (4.62)	1588.7 (15.3)	1043.6 (10.8)	983.1 (7.90)	1082.9 (9.28)	0
DATSUN	14. Part. Filtration		I	6.0	–	–	–	–	–	–	807.9 (7.73)	758.6 (7.88)	–	–	–
	15. Mut. Bkgd.		dk	0.5	NEG	48.1 (0.31)	235.2 (2.19)	336.7 (3.34)	477.7 (4.36)	691.6 (6.22)	2822.9 (19.5)	1549.9 (15.4)	1256.6 (10.5)	1445.4 (12.6)	0
	16. Part. Filtration		I	6.0	–	–	–	–	–	–	1484.1 (13.8)	1886.1 (16.4)	840.8 (6.93)	1210.8 (10.66)	–
	18. Diesel Exhaust		I	24	–	–	–	–	–	–	1198.8 (10.5)	1068.8 (9.44)	773.4 (6.35)	838.8 (7.08)	–
	19. Increase Propylene	SET 2	I	24	–	–	–	289.7 (2.82)	956.5 (7.35)	1184.3 (9.50)	–	859.8 (8.34)	868.8 (6.83)	1037.3 (8.45)	–
	21. Part. Filtration		I	6.0	–	–	–	287.2 (2.71)	–	–	–	981.8 (9.70)	911.7 (7.88)	1127.4 (8.96)	–
	22. Repeat #19		I	24	NEG	58.2 (0.29)	–	296.8 (2.53)	1730.2 (15.9)	1911.4 (17.9)	–	973.8 (9.48)	912.8 (7.05)	988.8 (7.78)	–
	24. Diesel Exhaust		I	6.0	–	–	–	328.6 (3.39)	–	–	–	940.7 (9.44)	873.1 (4.89)	1150.8 (9.93)	–
	25. Diesel Exhaust		I	24	–	–	–	98.5 (0.98)	–	–	–	292.2 (2.52)	309.1 (1.39)	422.8 (2.87)	—
	26. w/o Prim. Part.		I	24	–	–	–	48.8 (0.46)	–	–	–	150.9 (1.24)	235.7 (0.88)	271.3 (1.04)	—
	28. Prop/SO_2/NO_x		I	6.0	NEG	NEG	–	53.2 (0.42)	383.7 (2.88)	415.9 (3.79)	NEG	NEG	254.7 (1.35)	309.0 (1.58)	—
	29. Prop/SO_2/NO_x		I	24	–	–	–	NEG	–	–	–	55.8 (0.26)	–	–	Nil Response
MERCEDES	32-1 Double		dk	0.5	NEG	NEG	224 (2.02)	351 (3.51)	415 (3.87)	599 (5.67)	1320 (10.9)	1080 (10.1)	1346 (11.4)	1074 (8.91)	0
	32-2 Mutagenic		dk	6.0	NEG	NEG	271 (2.28)	406 (3.97)	575 (5.39)	732 (6.96)	1891 (17.7)	1656 (13.4)	1724 (14.8)	1137 (9.56)	+
	33. High O_3		dk	6.0	–	–	143 (1.29)	144 (1.35)	324 (2.58)	328 (3.01)	938 (7.28)	836 (7.74)	606 (3.62)	532 (3.56)	–
	34-1 Tailpipe Sample		dk	0	–	–	1163 (11.4)	1707 (16.8)	–	–	3444 (31.3)	5874 (56.1)	1761 (15.5)	1768 (15.6)	++
	34-2 Hi-vol Sample		dk	0.5	–	–	208 (1.94)	275 (2.99)	434 (4.11)	548 (5.22)	1582 (15.0)	1466 (13.2)	–	1064 (9.20)	0
	36. Diesel Exhaust	SET 3	I	6.0	–	–	77 (0.54)	188 (1.85)	–	–	450 (2.96)	1029 (9.73)	502 (3.38)	724 (5.64)	–
	37. Toluene		I	6.0	–	–	85 (0.41)	98 (0.81)	–	–	361 (2.25)	857 (6.23)	423 (2.84)	516 (3.82)	–
	40. Low SO_2		I	6.0	–	–	59 (0.29)	144 (1.30)	–	–	278 (1.88)	837 (6.23)	404 (2.38)	559 (4.29)	–
	43. Diesel Exhaust		I	6.0	–	–	84 (0.52)	154 (1.29)	–	–	534 (4.84)	785 (7.28)	473 (2.38)	588 (4.35)	–
	44-1 Double		dk	0.5	–	–	195 (1.55)	299 (3.15)	–	–	1284 (10.3)	1489 (13.4)	1351 (11.7)	748 (5.89)	0
	44-2 Mutagenic		I	6.0	–	–	262 (2.14)	387 (2.92)	412 (3.41)	600 (5.43)	1385 (11.0)	2002 (19.1)	1182 (9.41)	1179 (10.1)	+
MERCEDES	51. Diesel/Gas 10% Diesel		I	6.0	–	–	–	–	–	–	553 (3.90)	288 (2.50)	585 (4.70)	304 (1.70)	
	53. Diesel/Gas 40% Diesel		I	6.0	–	–	–	–	–	–	1362 (13.2)	1178 (9.00)	729 (3.20)	643 (2.20)	
	56. Diesel/Gas 40% Diesel	SET 4	I	6.0	–	–	–	–	–	–	1899 (18.8)	1778 (17.1)	827 (7.00)	867 (7.50)	
	57. Diesel/Gas 40% Diesel		I	6.0	–	–	–	–	–	–	2139 (21.0)	1943 (19.0)	977 (9.50)	838 (7.20)	
	58. Diesel/Gas w/o Prim. Port.		I	6.0	–	–	–	–	–	–	176 (0.90)	184 (1.10)	178 (0.50)	162 (0.40)	
	59. Diesel/Gas with NH_3		I	6.0	–	–	–	–	–	–	589 (4.00)	939 (7.70)	581 (4.60)	–	

* dk = Nonirradiated; I = Irradiated
**NEG = No Response
† Change in Mutagenicity: 0 = None; – = Decrease; — = Large Decrease; + = Increase; ++ = Large Increase

ozone was added to dilute diesel emissions also revealed a decrease in mutagenic activity of the diesel emissions (experiments #33 compared to #31-1). Consequently, ozone is believed to be at least partly responsible for the observed decrease in mutagenicity of the irradiated diesel emission + reactive hydrocarbon system. This could be due to: (1) reactions forming higher vapor pressure compounds; or, (2) reactions leading to less responsive aerosols.

Aerosol samples of photochemically generated aerosols from irradiated, primary particle-free systems were bioassayed to supply data on the production of mutagenic aerosol species by photochemical processes. Two types of systems were investigated: (1) diluted diesel emission/propylene systems (without diesel primary particules); and, (2) propylene/SO_2/NO_x systems. The mutagenic activities of the photochemical aerosols generated in both of these systems were much lower than those of the aerosol samples of irradiated diluted diesel emission/propylene systems which contained the diesel primary particulates (compare experiments 12, 26, 28 and 29 with 22 and 24). In addition, the similarity of the mutagenic activities of the photochemical aerosols generated by irradiation of the two distinct primary particle-free systems suggested that the same reactions were responsible for producing the mutagenic activity of both systems. While the level of mutagenic activity of the photochemically generated aerosol was relatively low for these particular systems, these data demonstrate that atmospheric processes do exist for these particular systems which may be responsible for generating compounds of significant mutagenic activity.

One sample of diesel emission particulates was collected with a high surface area, low pressure drop filter located in-line with and very near the auto exhaust (experiment #34). A low level of extractables contained in this sample was attributed to the high temperature of the filter during collection. The mutagenic activity of this sample on a per-weight basis was very high. Two possible explanations are offered for the observed high mutagenicity: (1) the small fraction of highest molecular weight organics collected at the high temperatures represent the most significant mutagenic component of the diesel emissions (at ambient temperatures, other condensible organics are less mutagenic and essentially dilute these); or (2) the high

temperatures at which the sample was obtained resulted in the chemical transformation of the organic compounds to produce a new compound which exhibited a greater mutagenic activity.

The mutagenic activities associated with aerosol samples collected from experiments #50-60 are presented in Table 3 for completeness. However, these results were not included in the above discussions due to the availability of data for only two strains of bacteria and to the lack of any data for critical experiments (#52 and 54).

In summary, the following trends in the mutagenic activity of the diesel emission aerosol were indicated:

- The mutagenic activity of the diesel emissions consistently increased with containment in the dark.
- Irradiation in the absence of reactive hydrocarbons did not appear to be effective in reducing the mutagenic activity of diesel emissions.
- The presence of reactive hydrocarbons which led to significant ozone formation in irradiated diesel emission systems resulted in reduced mutagenic activity.
- The presence of ozone appeared to reduce the mutagenic activity of diesel emissions.
- Photochemical aerosol produced by irradiation of $HC/SO_2/NO_x$ and diesel emission/HC systems (without diesel primary particulates) exhibited significant mutagenic activity.
- The aerosol collected on an in-line filter near the exhaust of a diesel auto (at high temperature) contained low levels of extractables and exhibited a very high mutagenic activity.

A preliminary interpretation of the results of the mutagenic testing in this program and a detailed description of the analytical technique were presented at the Symposium on Health Effects of Diesel Engine Emissions (Claxton and Barnes, 1979).

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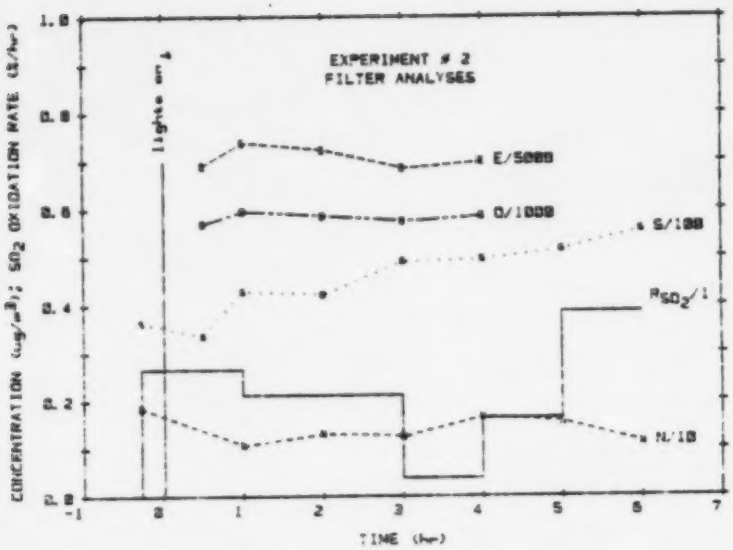
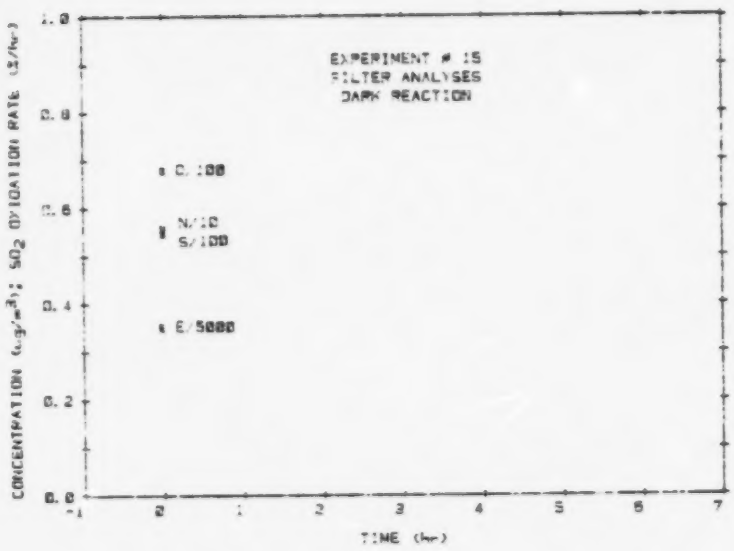
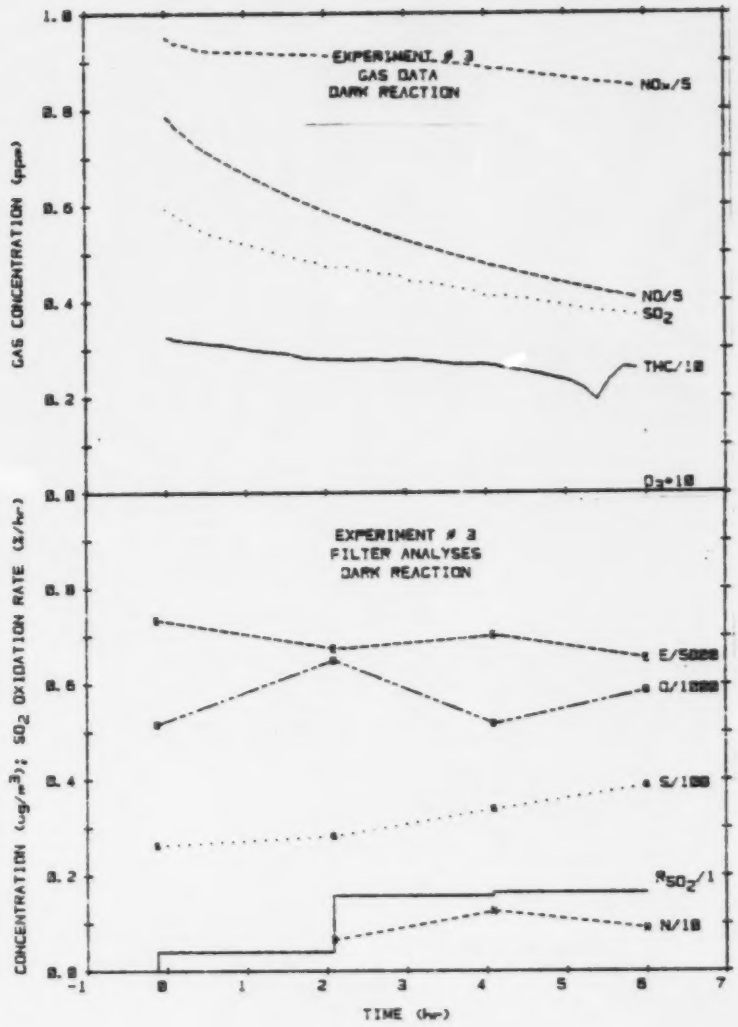
Appendix A

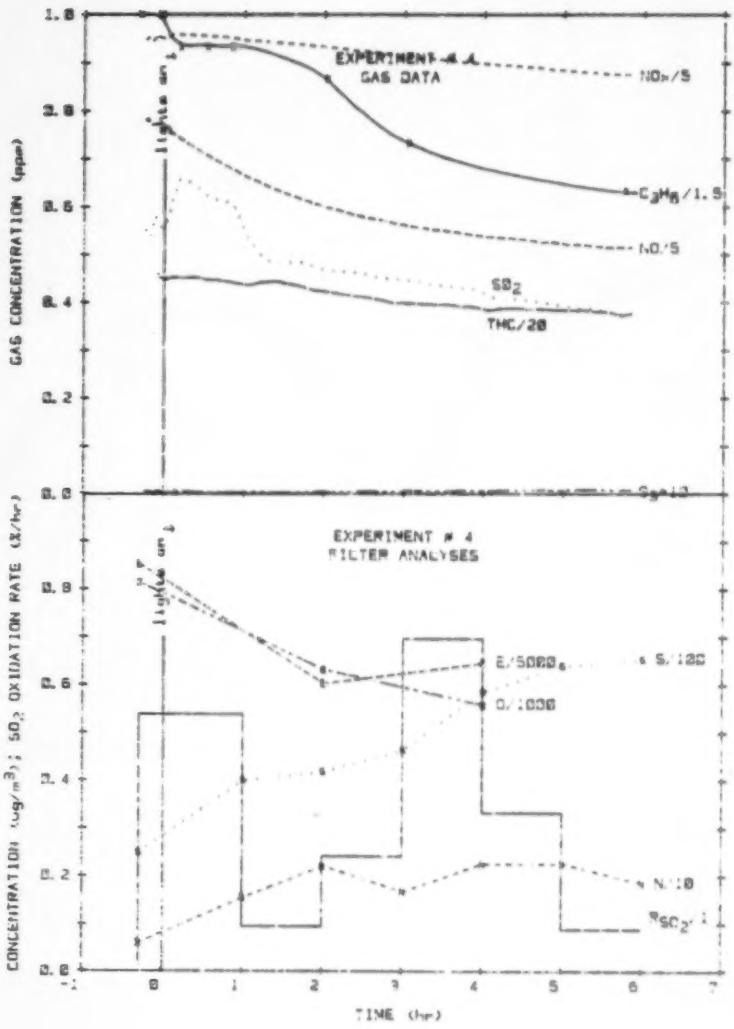
Gas, Aerosol, and Chemical Analyses Data

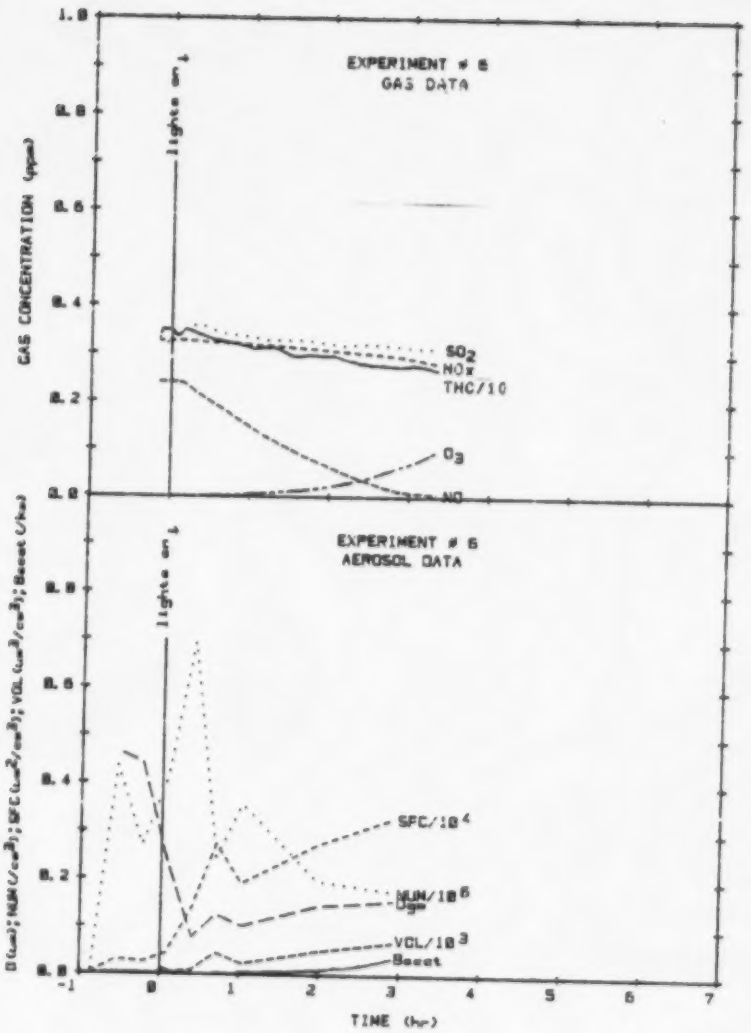
Following are graphical presentations of the gas, aerosol, and chemical analyses data (where available) plotted against time for each applicable experiment. Aerosol data consist of the number (NUM), surface area (SFC), and volume (VOL) of the aerosol per cubic centimeter of chamber volume, the geometric mass mean diameter (Dgm), and the scattering coefficient (B_{scat}). The aerosol data are presented in units of the appropriate power of microns. B_{scat} is presented in inverse kilometers. Gas data include the concentration of O_3, SO_2, NO, NO_x, total hydrocarbons (THC), and propylene (C_3H_6). Except for THC which is presented in parts per million carbon, the units of the gas data are parts per million. Chemical analyses of filter samples provided the concentration (micrograms per cubic meter) of sulfates (S), nitrates (N), carbon in the form of elemental (E) and organic (O), and the rate of SO_2 oxidation (R_{SO_2}) in percent per hour as determined from sulfate formation and the available SO_2. The time of the initiation of irradiation is denoted by a vertical line labeled 'Lights on'.

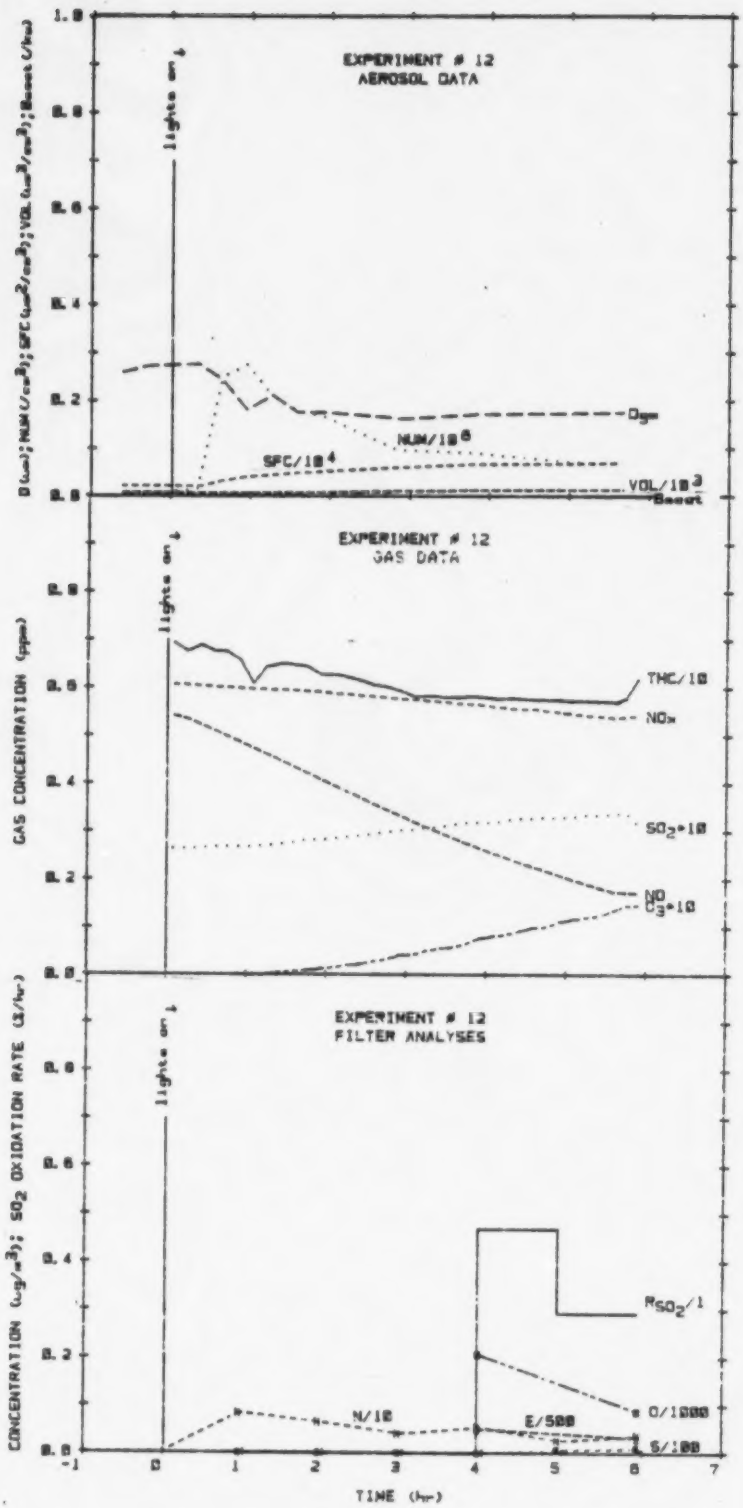

EXPERIMENT # 2
FILTER ANALYSES
lights on
E/5000
O/1000
S/100
$R_{SO_2}/1$
N/10
TIME (hr)

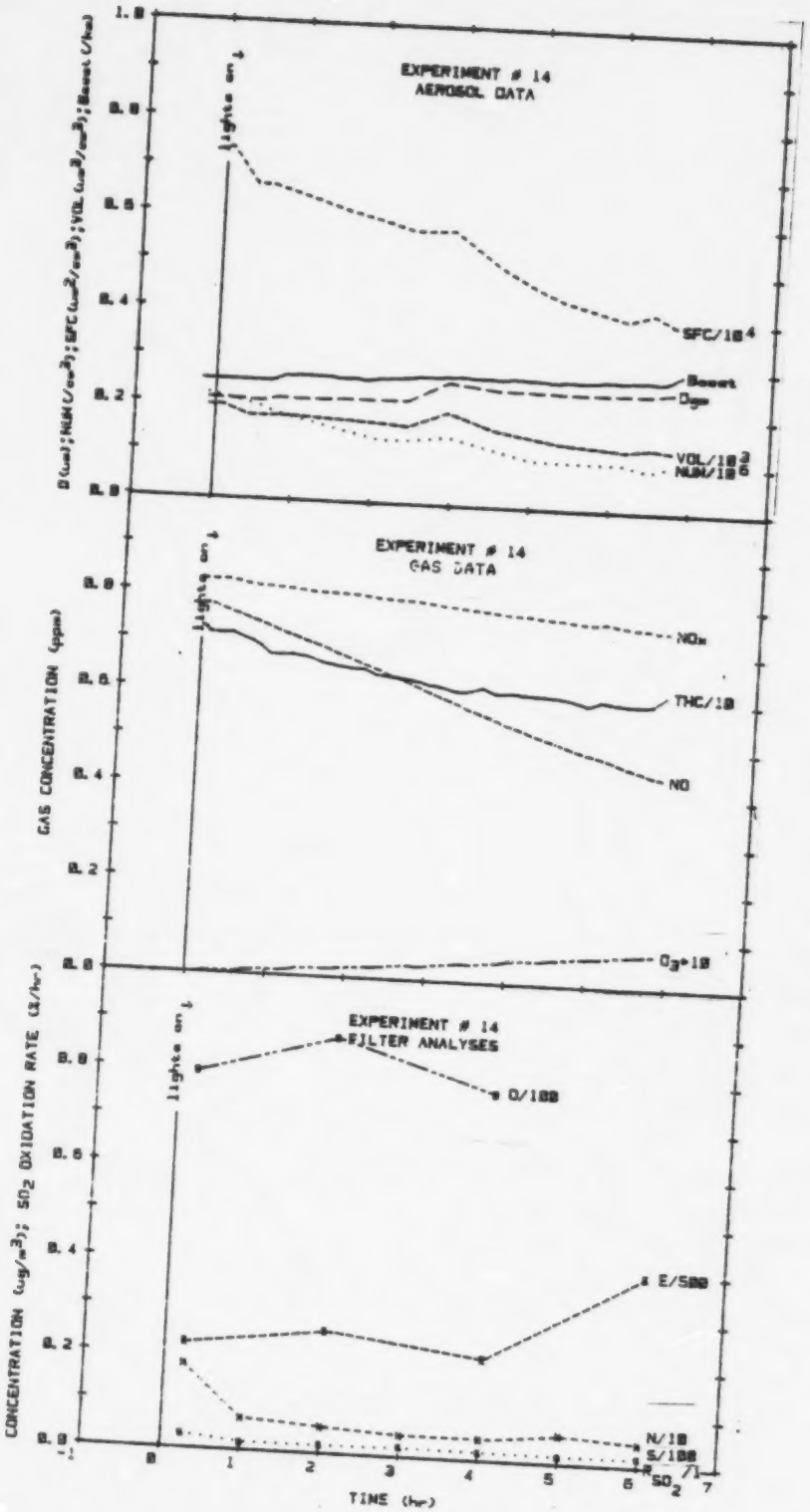

EXPERIMENT # 15
FILTER ANALYSES
DARK REACTION
O/100
N/10
S/100
E/5000
TIME (hr)

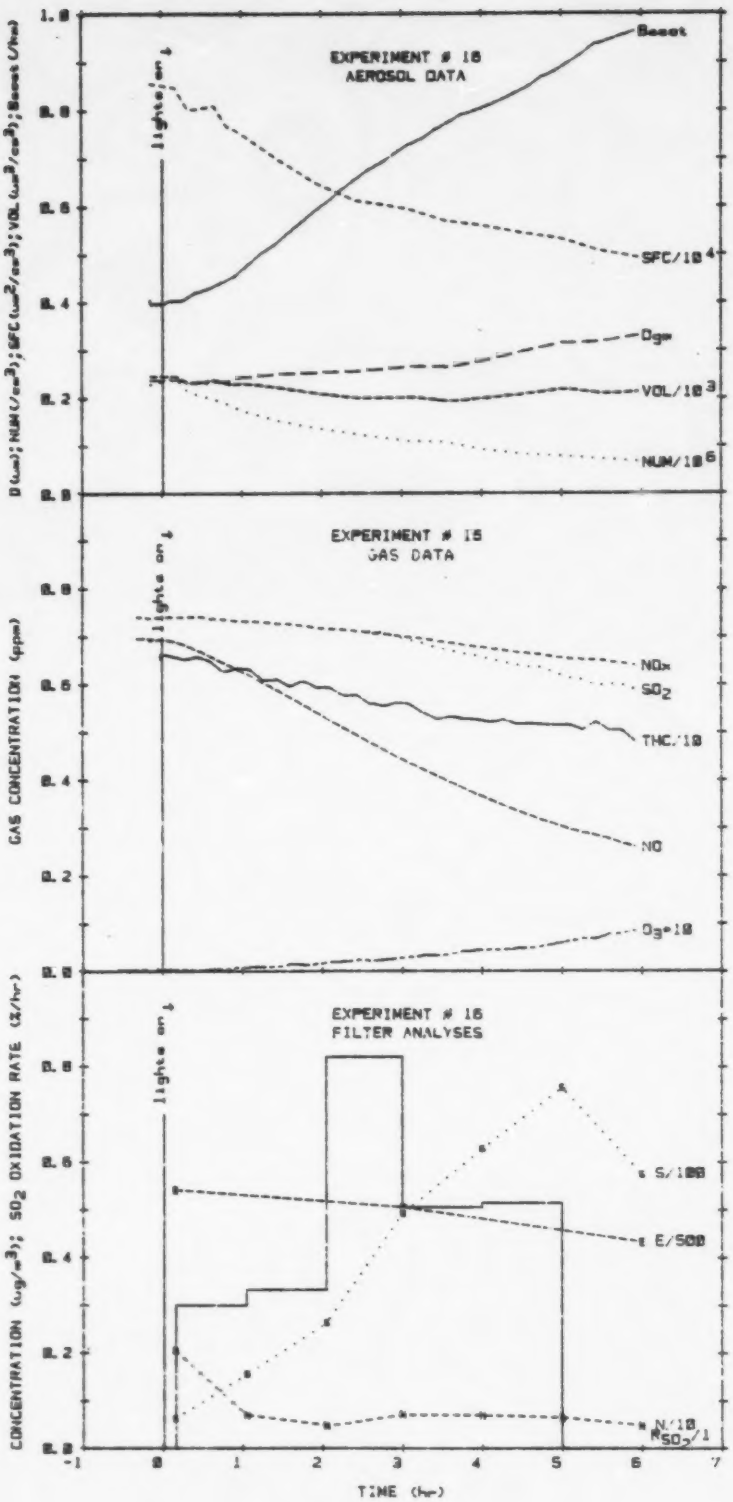

EXPERIMENT # 3
GAS DATA
DARK REACTION
NOx/5
NO/5
SO2
THC/10
O3*10
GAS CONCENTRATION (ppm)
EXPERIMENT # 3
FILTER ANALYSES
DARK REACTION
E/5000
O/10000
S/100
RSO2/1
N/10
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
TIME (hr)

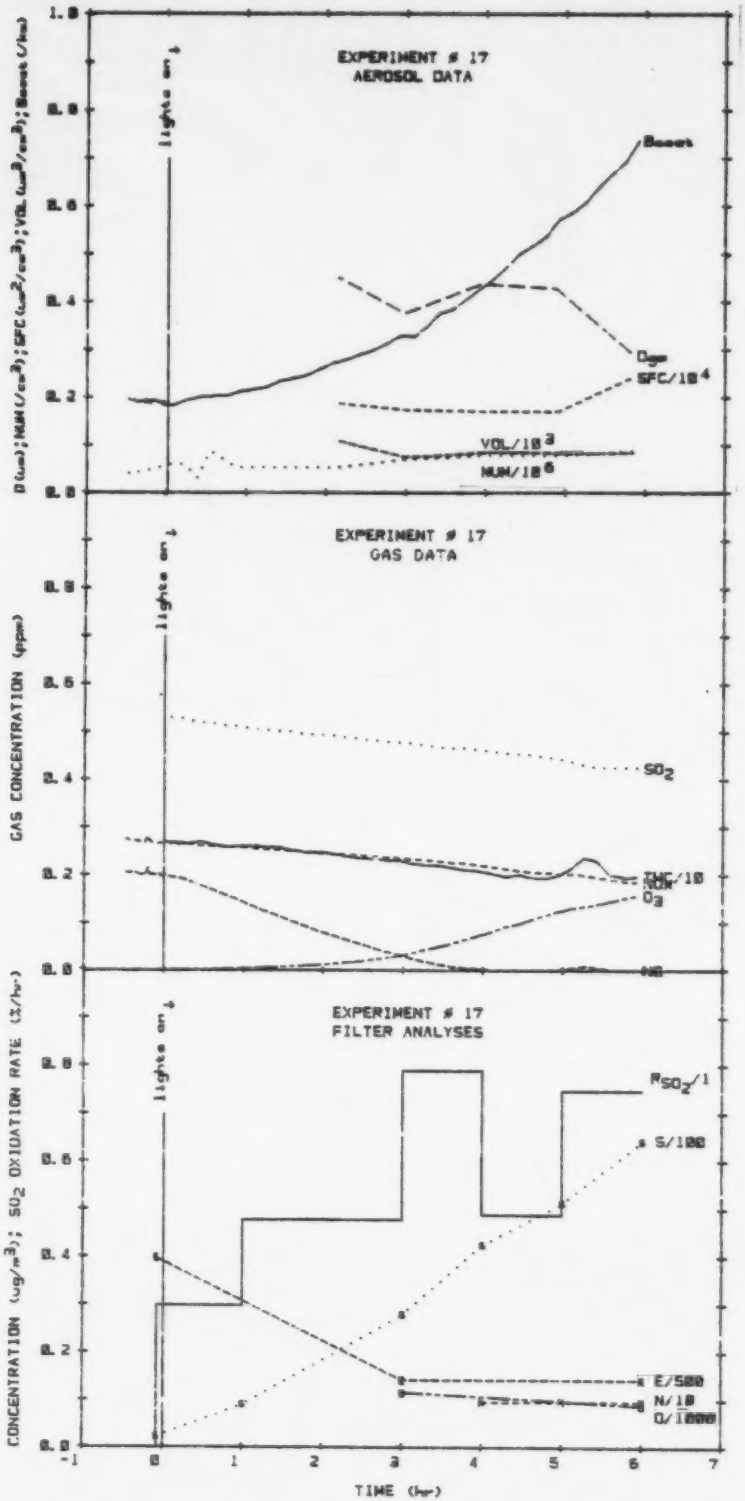

EXPERIMENT # 4
GAS DATA
NOx/5
C3H8/1.5
NO/5
SO2
THC/20
EXPERIMENT # 4
FILTER ANALYSES
S/120
O/1000
N/10
GAS CONCENTRATION (ppm)
TIME (hr)

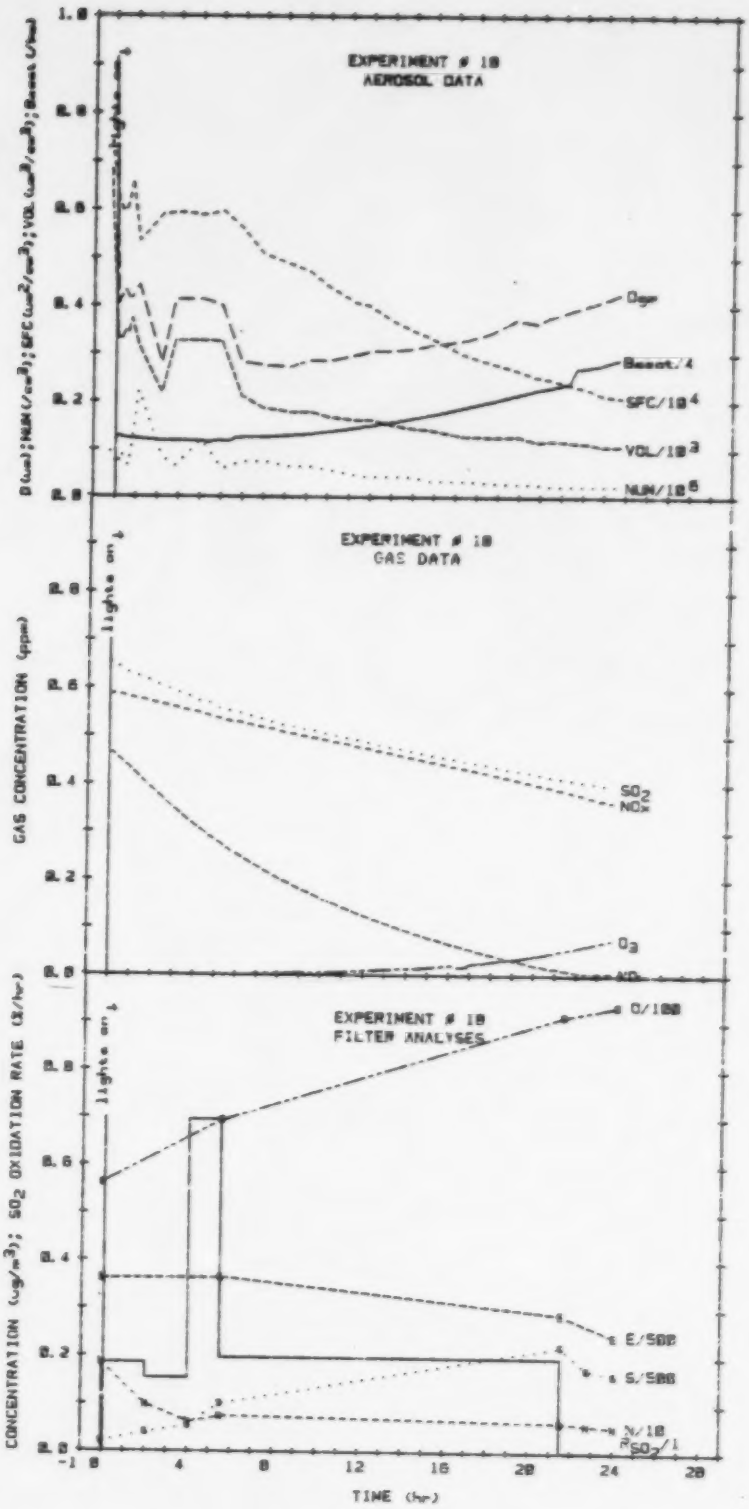

EXPERIMENT # 6
GAS DATA
lights on
GAS CONCENTRATION (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
SO_2
NO_x
THC/10
O_3
NO
EXPERIMENT # 6
AEROSOL DATA
lights on
SFC/10^4
NUN/10^6
D_{sp}
VOL/10^3
Bscat
-1
0
1
2
3
4
5
6
7
TIME (hr)

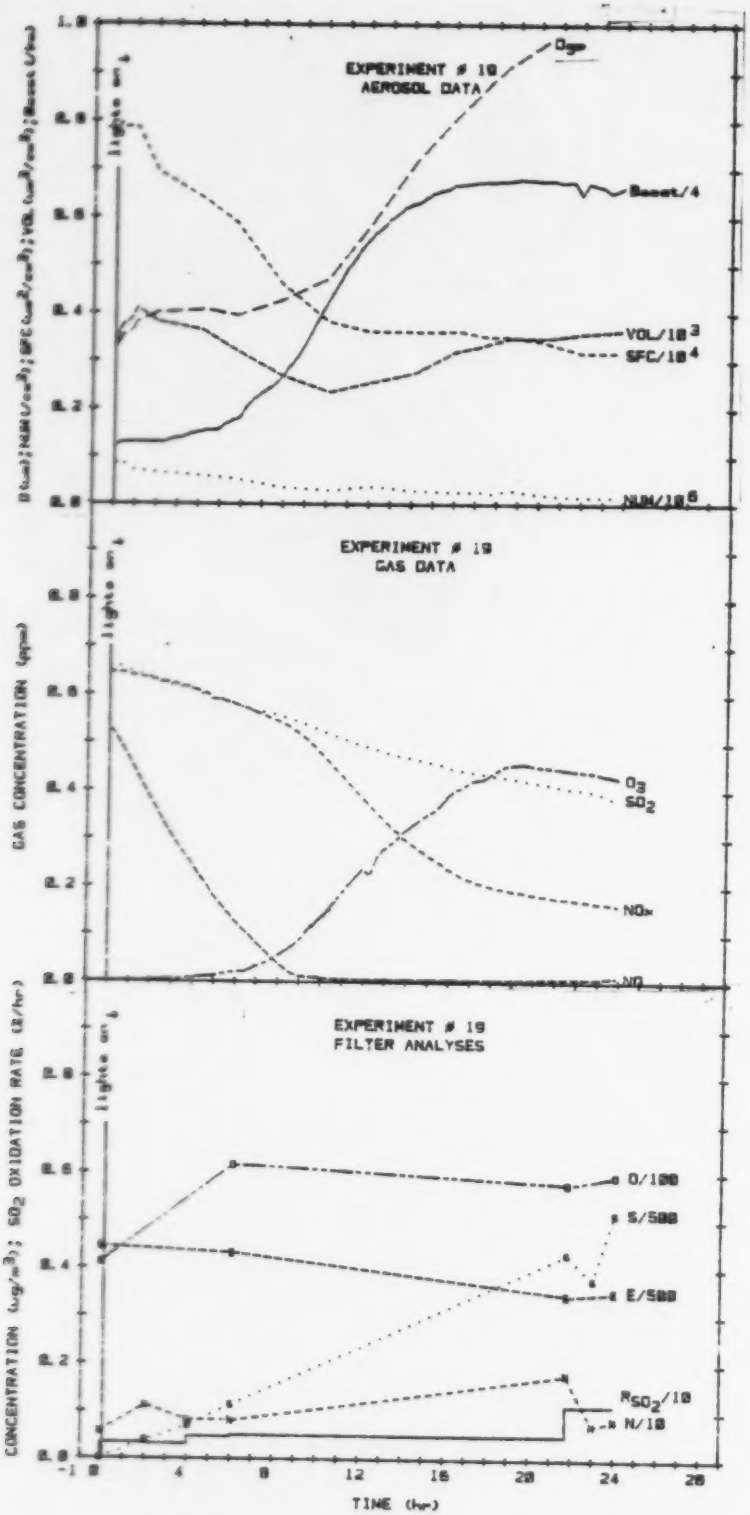

EXPERIMENT # 12
AEROSOL DATA
lights on
NUM/10^6
SFC/10^4
VOL/10^3
Bscat
EXPERIMENT # 12
GAS DATA
lights on
THC/10
NOx
SO2*10
NO
O3*10
EXPERIMENT # 12
FILTER ANALYSES
lights on
RSO2/1
O/1000
N/10
E/500
S/100
TIME (hr)

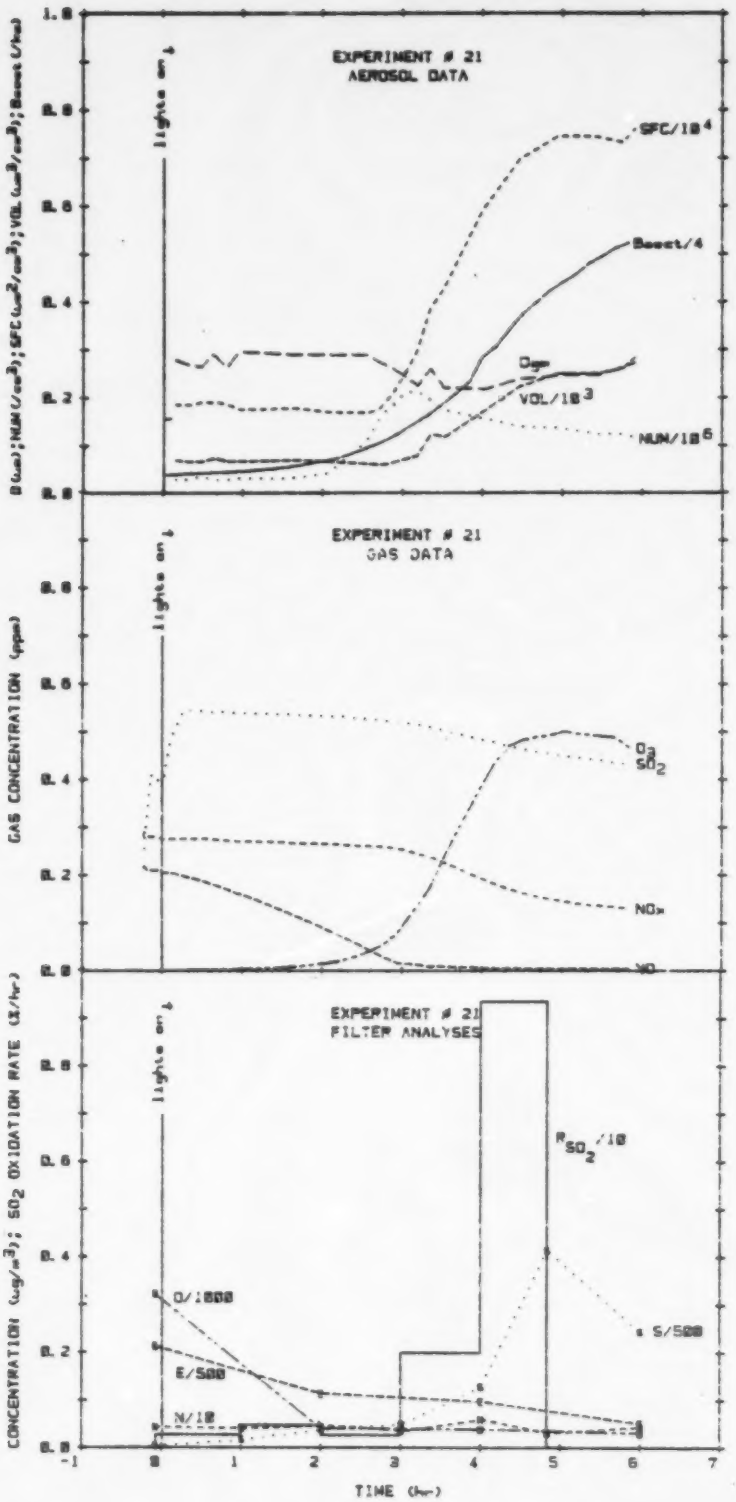

EXPERIMENT # 14
AEROSOL DATA
lights on
SFC/10^4
Bscat
Dgn
VOL/10^3
NUM/10^6
EXPERIMENT # 14
GAS DATA
lights on
NOx
THC/10
NO
O3*10
EXPERIMENT # 14
FILTER ANALYSES
lights on
O/100
E/500
N/10
S/100
SO2/10
TIME (hr)

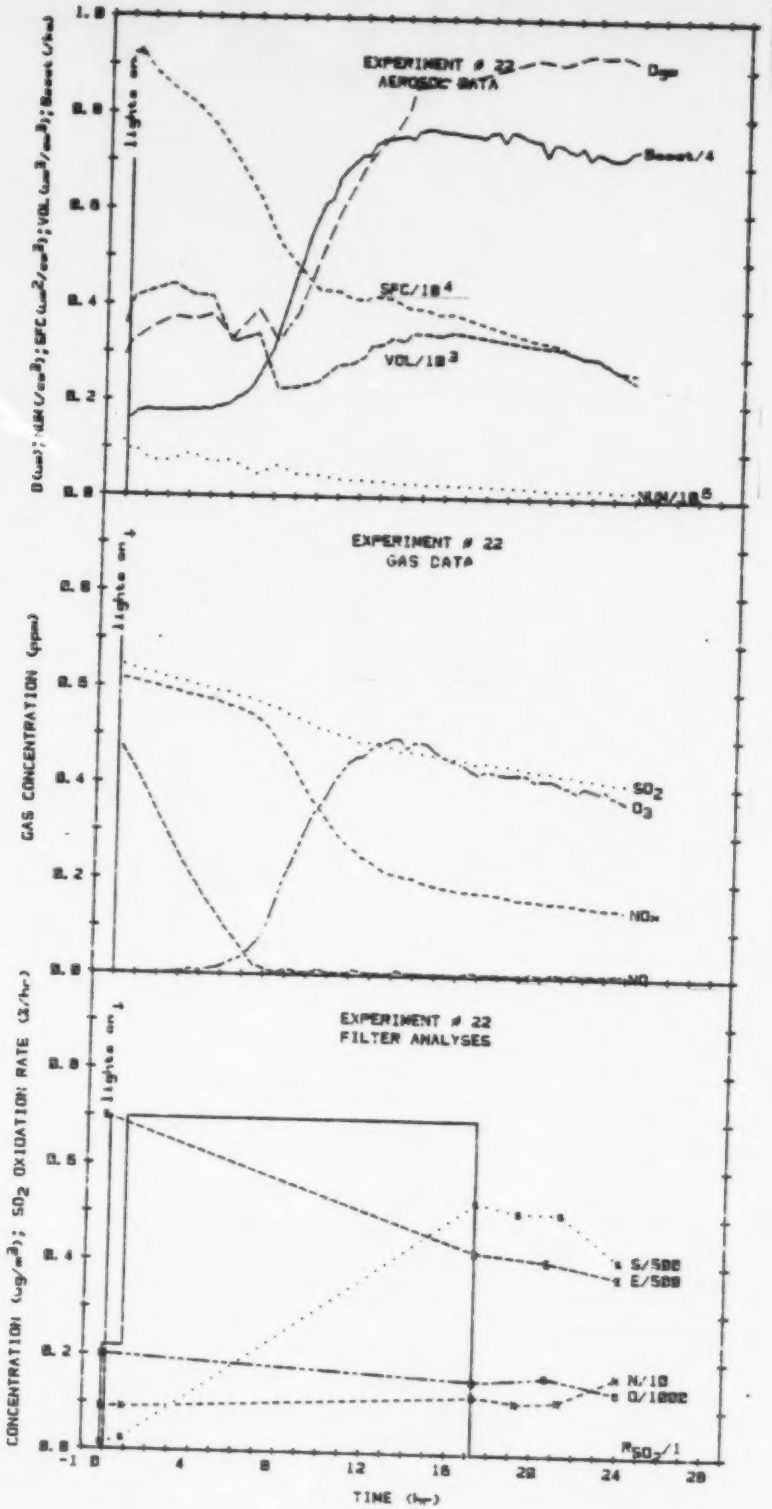

EXPERIMENT # 16
AEROSOL DATA
lights on
Bscat
SFC/10^4
Dgw
VOL/10^3
NUM/10^6
EXPERIMENT # 16
GAS DATA
lights on
NOx
SO2
THC/10
NO
O3*10
EXPERIMENT # 16
FILTER ANALYSES
lights on
S/100
E/500
N/10
TIME (hr)

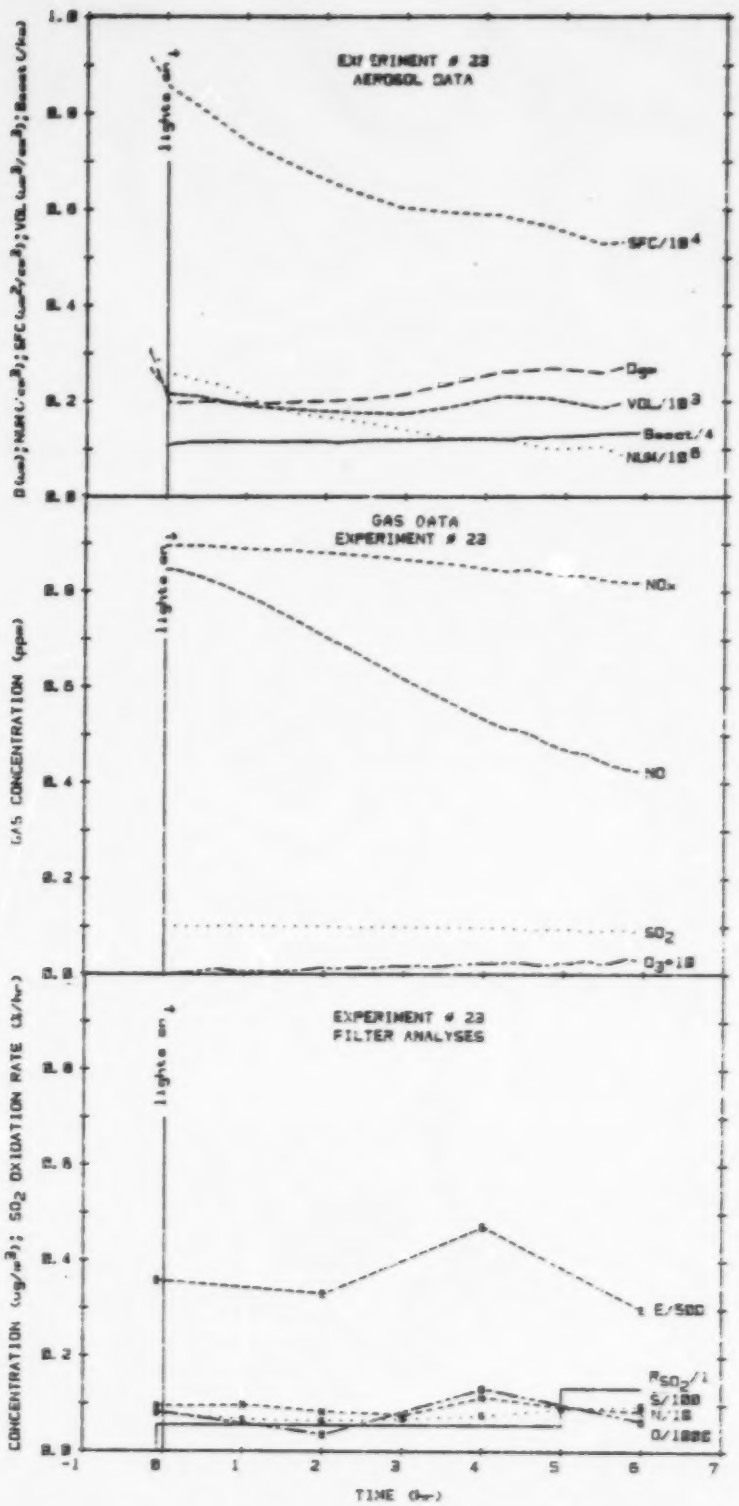

EXPERIMENT # 17
AEROSOL DATA
lights on
Bscat
Dgw
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 17
GAS DATA
lights on
SO2
THC/10
NOx
O3
EXPERIMENT # 17
FILTER ANALYSES
lights on
RSO2/1
S/100
E/500
N/10
O/1000
TIME (hr)

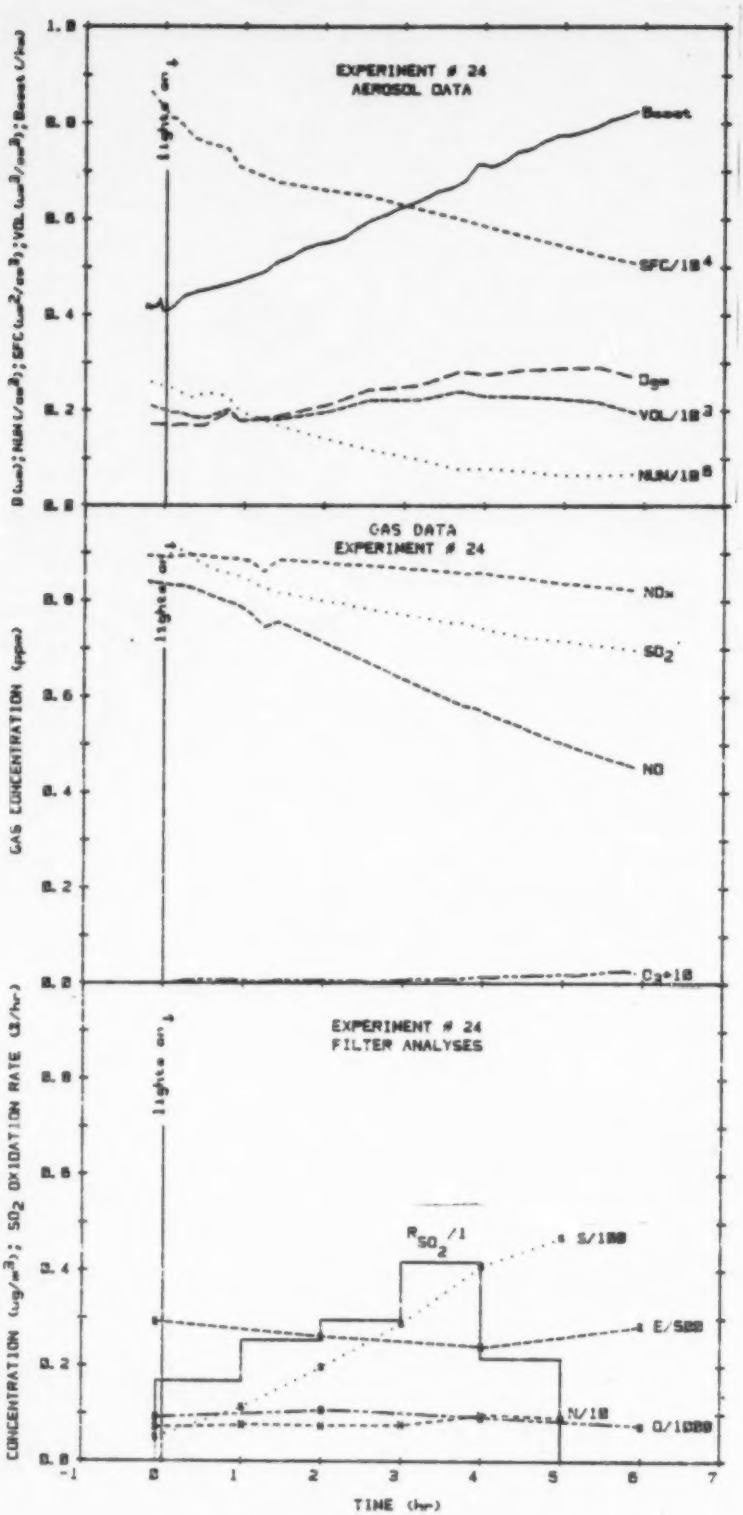

EXPERIMENT # 18
AEROSOL DATA
lights on
lights off
Dsp
Bscat/4
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 18
GAS DATA
GAS CONCENTRATION (ppm)
SO2
NOx
O3
NO
EXPERIMENT # 18
FILTER ANALYSES
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
O/100
E/500
S/500
N/10
rSO2/1
TIME (hr)

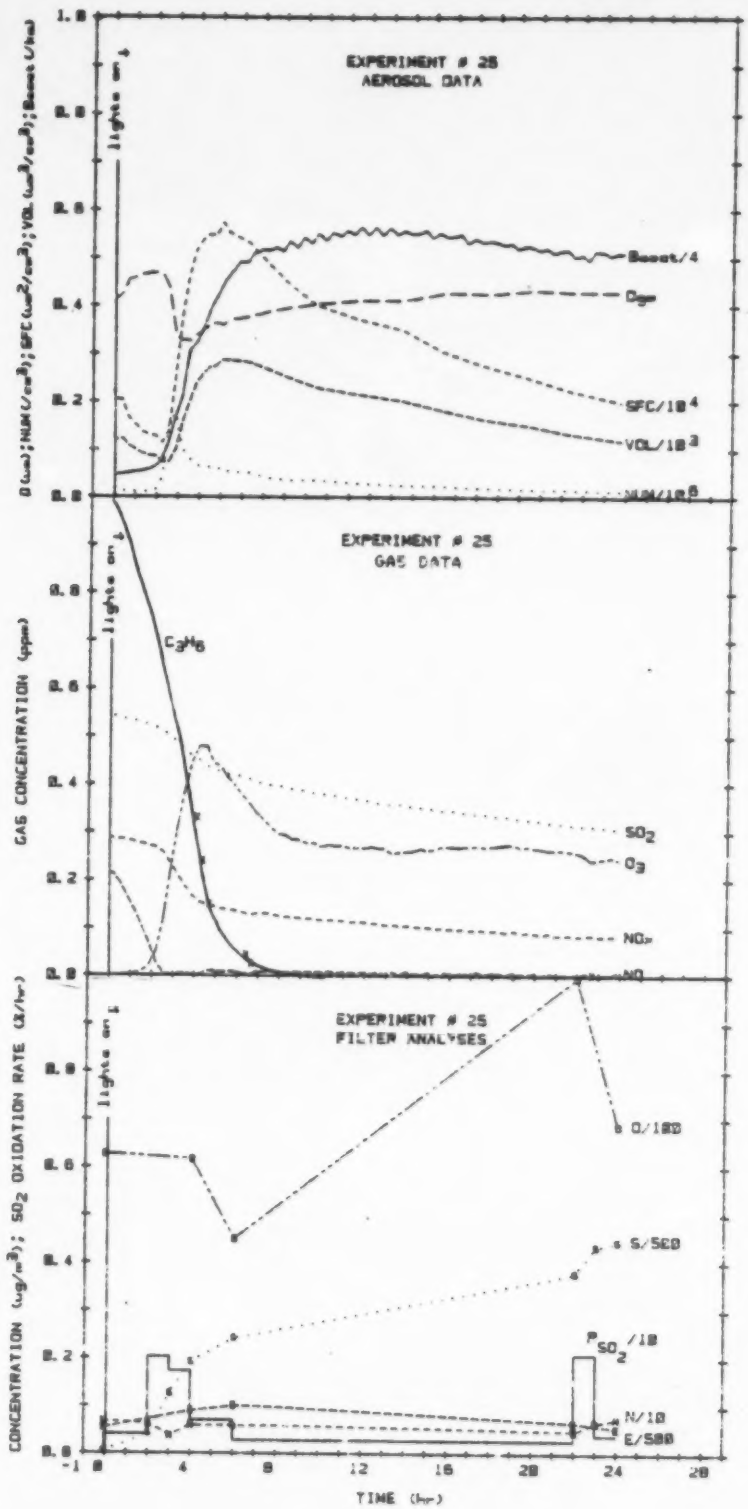

EXPERIMENT # 19
AEROSOL DATA
lights on
O_{gas}
Boost/4
VOL/10^3
SFC/10^4
NUM/10^6
EXPERIMENT # 19
GAS DATA
lights on
GAS CONCENTRATION (ppm)
O_3
SO_2
NO_x
NO
EXPERIMENT # 19
FILTER ANALYSES
lights on
CONCENTRATION ($\mu g/m^3$); SO_2 OXIDATION RATE (%/hr)
O/100
S/500
E/500
$R_{SO_2}/10$
N/10
TIME (hr)

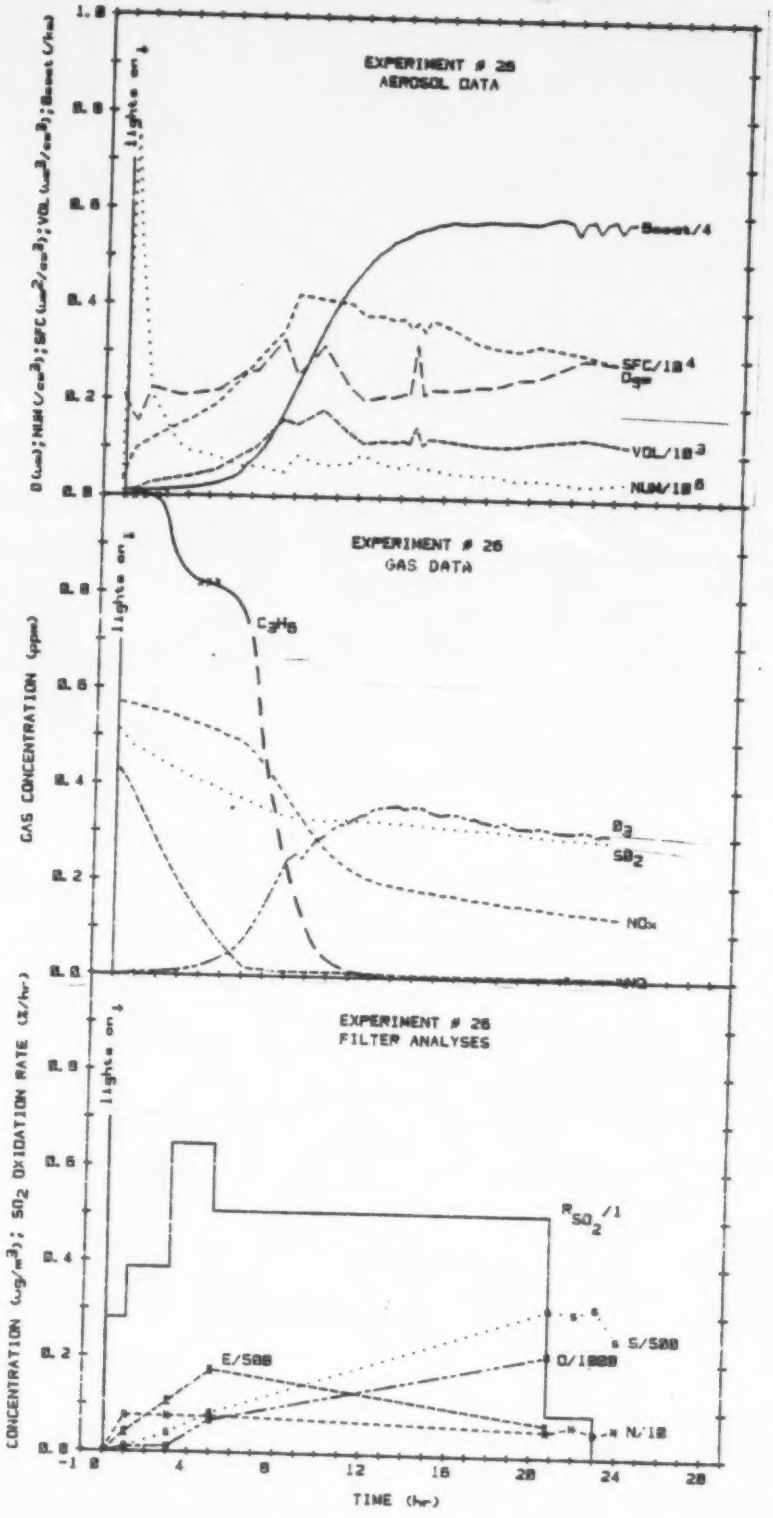

EXPERIMENT # 21
AEROSOL DATA
lights on
SFC/10^4
Bscat/4
Dgn
VOL/10^3
NUN/10^6
EXPERIMENT # 21
GAS DATA
lights on
O3
SO2
NOx
NO
GAS CONCENTRATION (ppm)
EXPERIMENT # 21
FILTER ANALYSES
lights on
R SO2 /10
O/1000
E/500
N/10
S/500
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
TIME (hr)

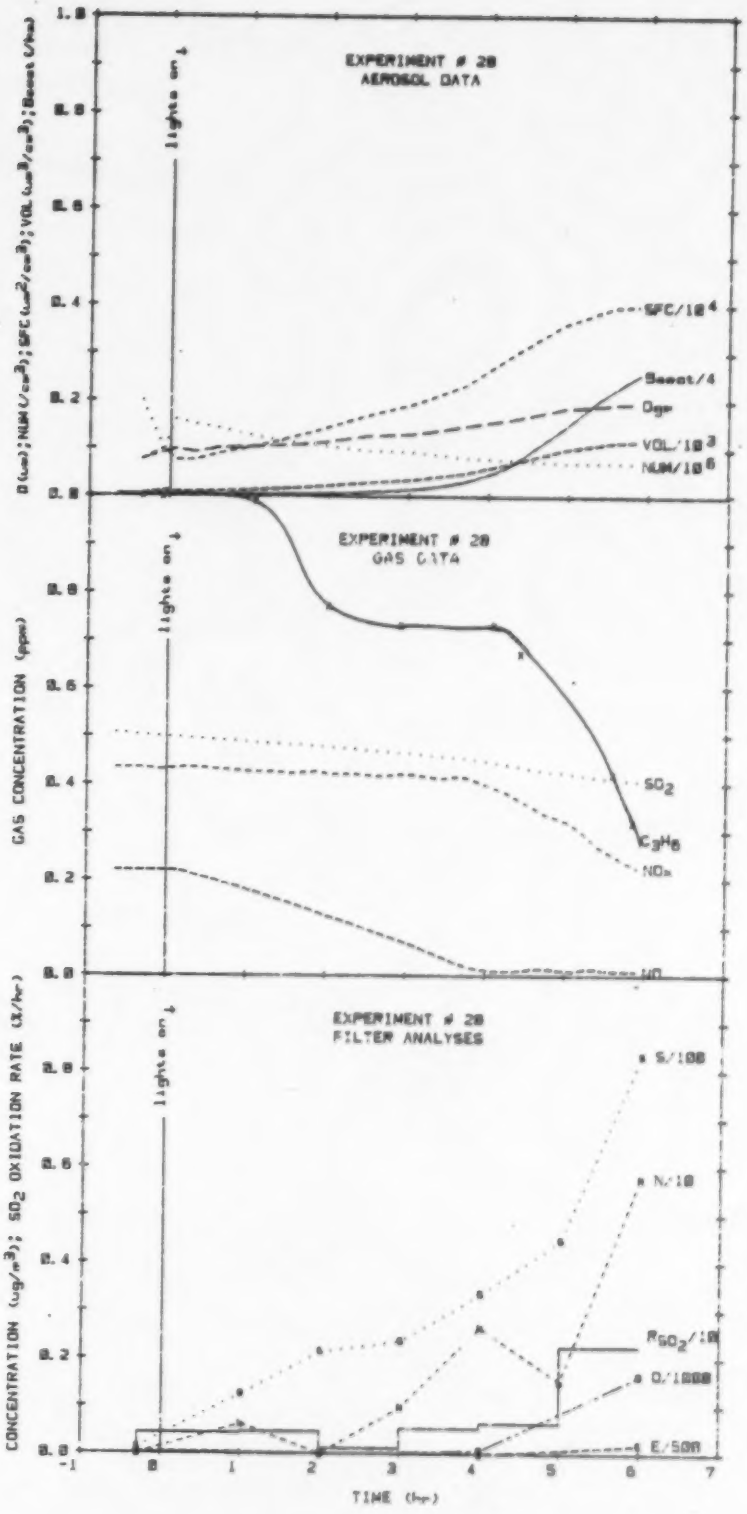

EXPERIMENT # 22
AEROSOL DATA
lights on
Bscat/4
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 22
GAS DATA
GAS CONCENTRATION (ppm)
lights on
SO2
O3
NOx
NO
EXPERIMENT # 22
FILTER ANALYSES
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
lights on
S/500
E/500
N/10
O/1000
RSO2/1
TIME (hr)

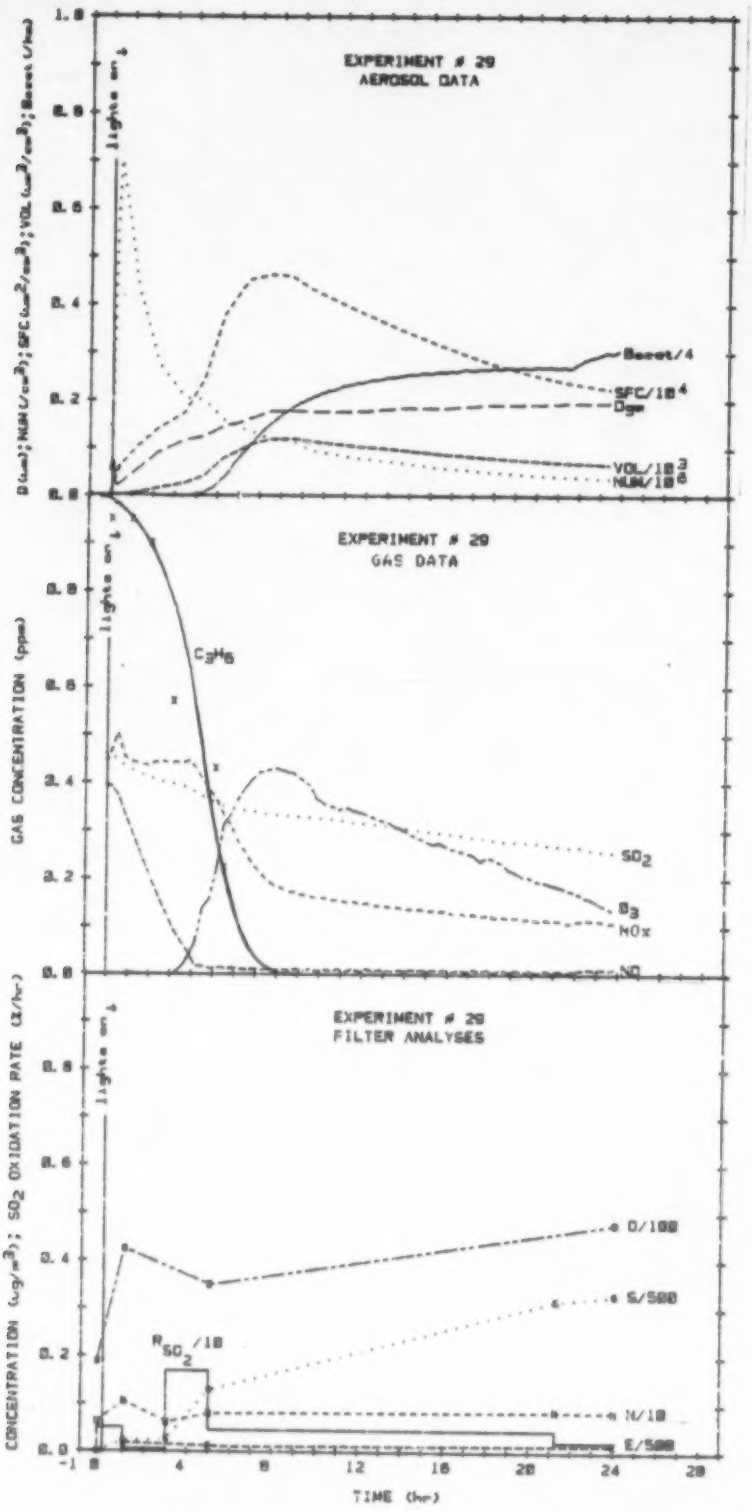

EXPERIMENT # 23
AEROSOL DATA
lights on
SFC/10^4
Dgp
VOL/10^3
Scat./4
NUM/10^6
GAS DATA
EXPERIMENT # 23
lights on
NOx
NO
SO2
O3*10
EXPERIMENT # 23
FILTER ANALYSES
lights on
E/500
S/100
N/10
O/1000
TIME (hr)

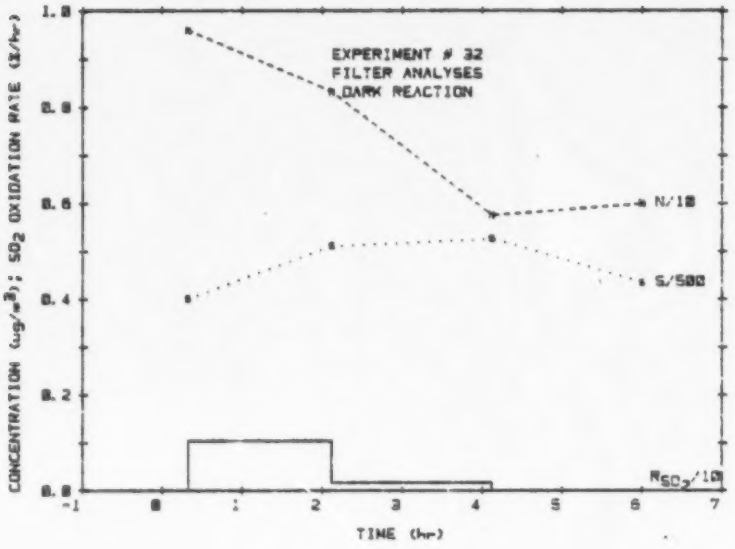

EXPERIMENT # 24
AEROSOL DATA
lights on
lights off
Bscat
SFC/10^4
Dgn
VOL/10^3
NUM/10^6
GAS DATA
EXPERIMENT # 24
NOx
SO2
NO
C2H2*10
EXPERIMENT # 24
FILTER ANALYSES
R SO2 /1
S/100
E/500
N/10
O/1000
GAS CONCENTRATION (ppm)
TIME (hr)

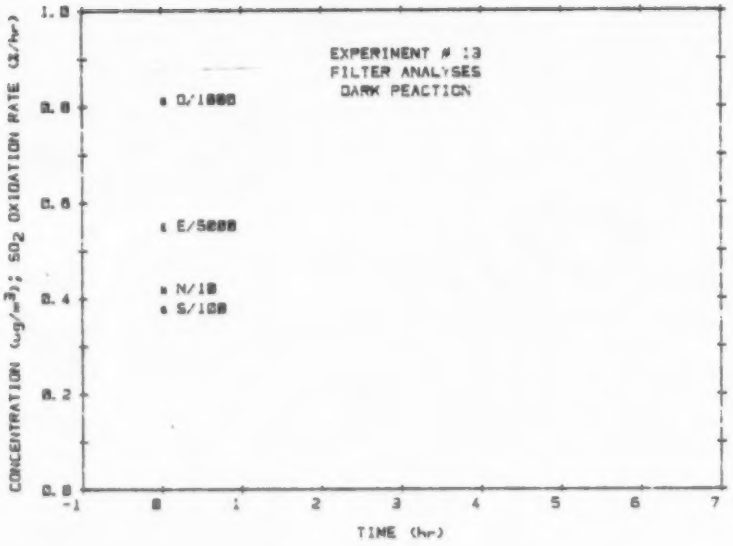

EXPERIMENT # 25
AEROSOL DATA
lights on
Bscat/4
Dgn
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 25
GAS DATA
lights on
C3H8
SO2
O3
NOx
NO
GAS CONCENTRATION (ppm)
EXPERIMENT # 25
FILTER ANALYSES
lights on
O/100
S/500
P_SO2/10
N/10
E/500
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
TIME (hr)

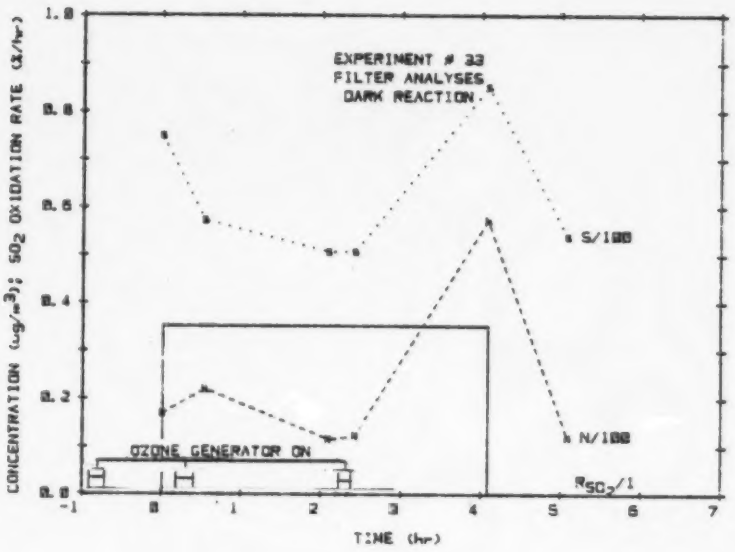

EXPERIMENT # 26
AEROSOL DATA
lights on
Bscat/4
SFC/10^4
D_ge
VOL/10^3
NUM/10^6
EXPERIMENT # 26
GAS DATA
lights on
C3H6
O3
SO2
NOx
NO
GAS CONCENTRATION (ppm)
EXPERIMENT # 26
FILTER ANALYSES
lights on
R_SO2/1
E/500
S/500
O/1000
N/10
CONCENTRATION (ug/m3); SO2 OXIDATION RATE (%/hr)
TIME (hr)

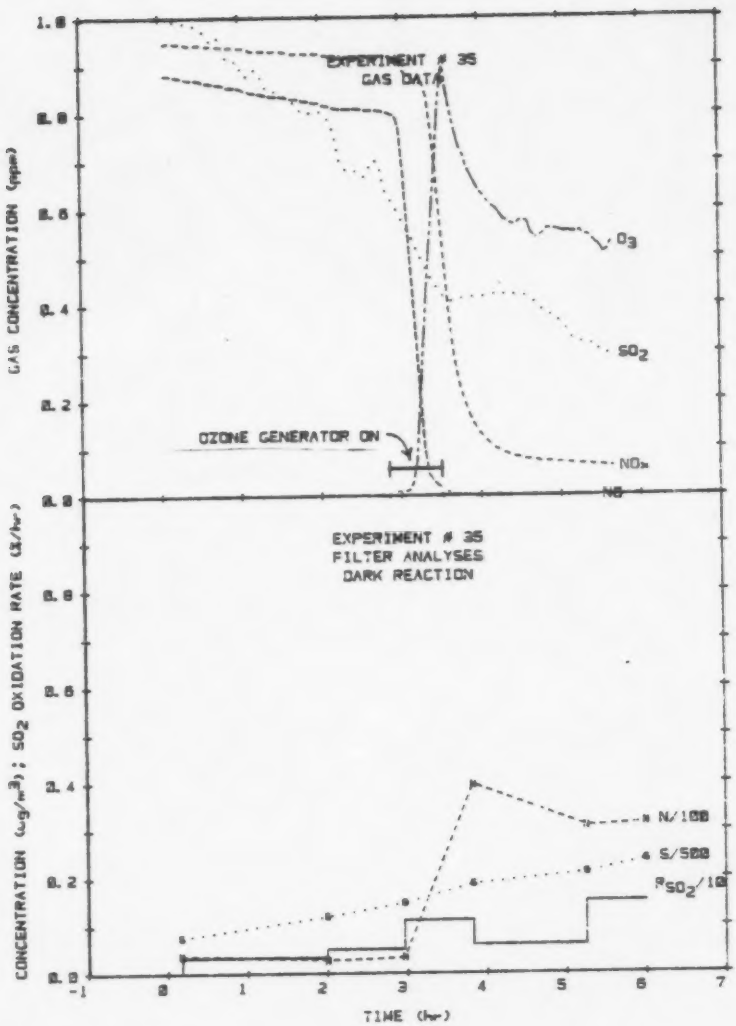

EXPERIMENT # 28
AEROSOL DATA
lights on
SFC/10^4
Soot/4
Dgp
VOL/10^3
NUM/10^6
EXPERIMENT # 28
GAS DATA
lights on
GAS CONCENTRATION (ppm)
SO2
C3H6
NOx
NO
EXPERIMENT # 28
FILTER ANALYSES
lights on
S/100
N/10
RSO2/10
O/1000
E/500
TIME (hr)

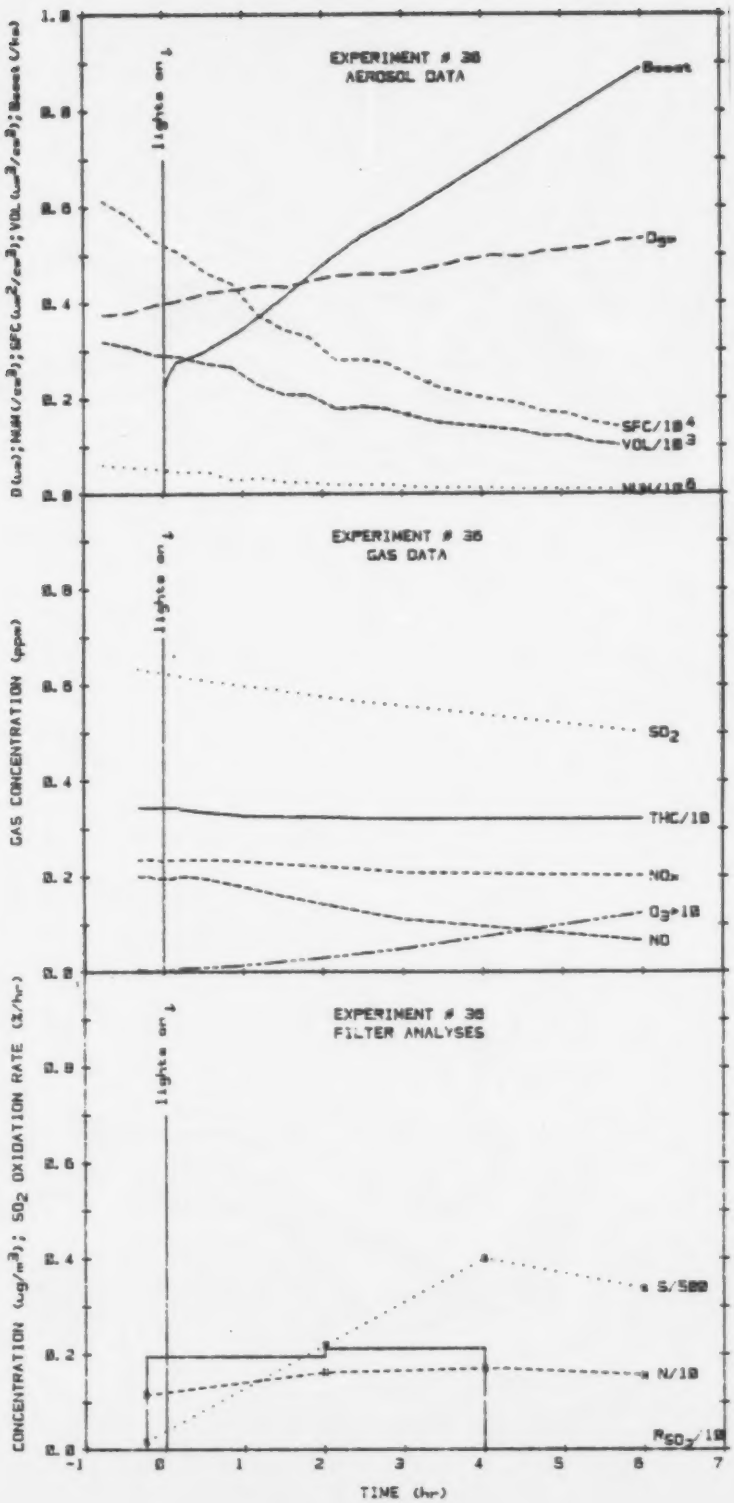

EXPERIMENT # 29
AEROSOL DATA
lights on
Dgn
Bscat/4
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 29
GAS DATA
lights on
C3H6
SO2
O3
HOx
NO
EXPERIMENT # 29
FILTER ANALYSES
lights on
O/100
S/500
N/10
E/500
R_SO2/10
TIME (hr)

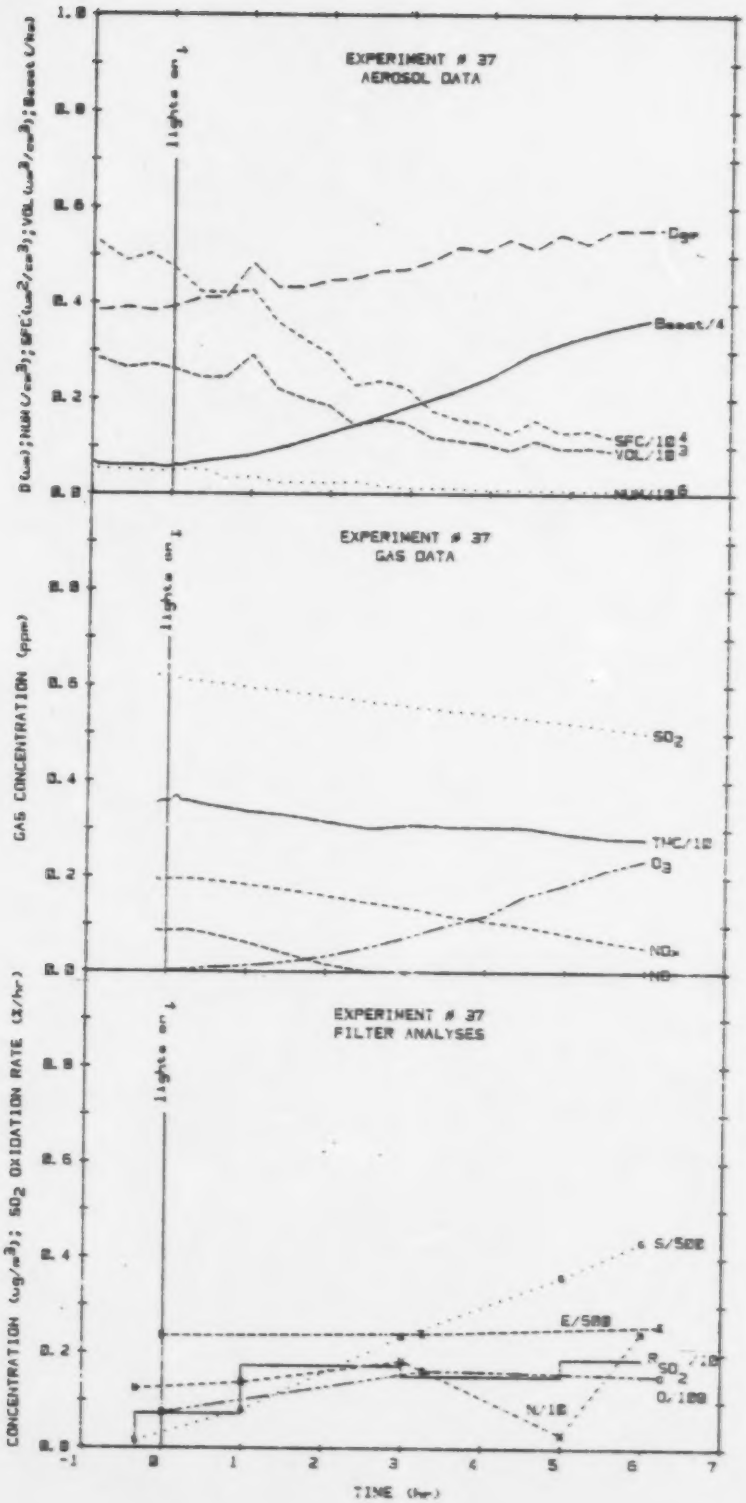

EXPERIMENT # 32
FILTER ANALYSES
DARK REACTION
N/18
S/500
R_{SO_2}/18
CONCENTRATION (ug/m³); SO_2 OXIDATION RATE (%/hr)
TIME (hr)

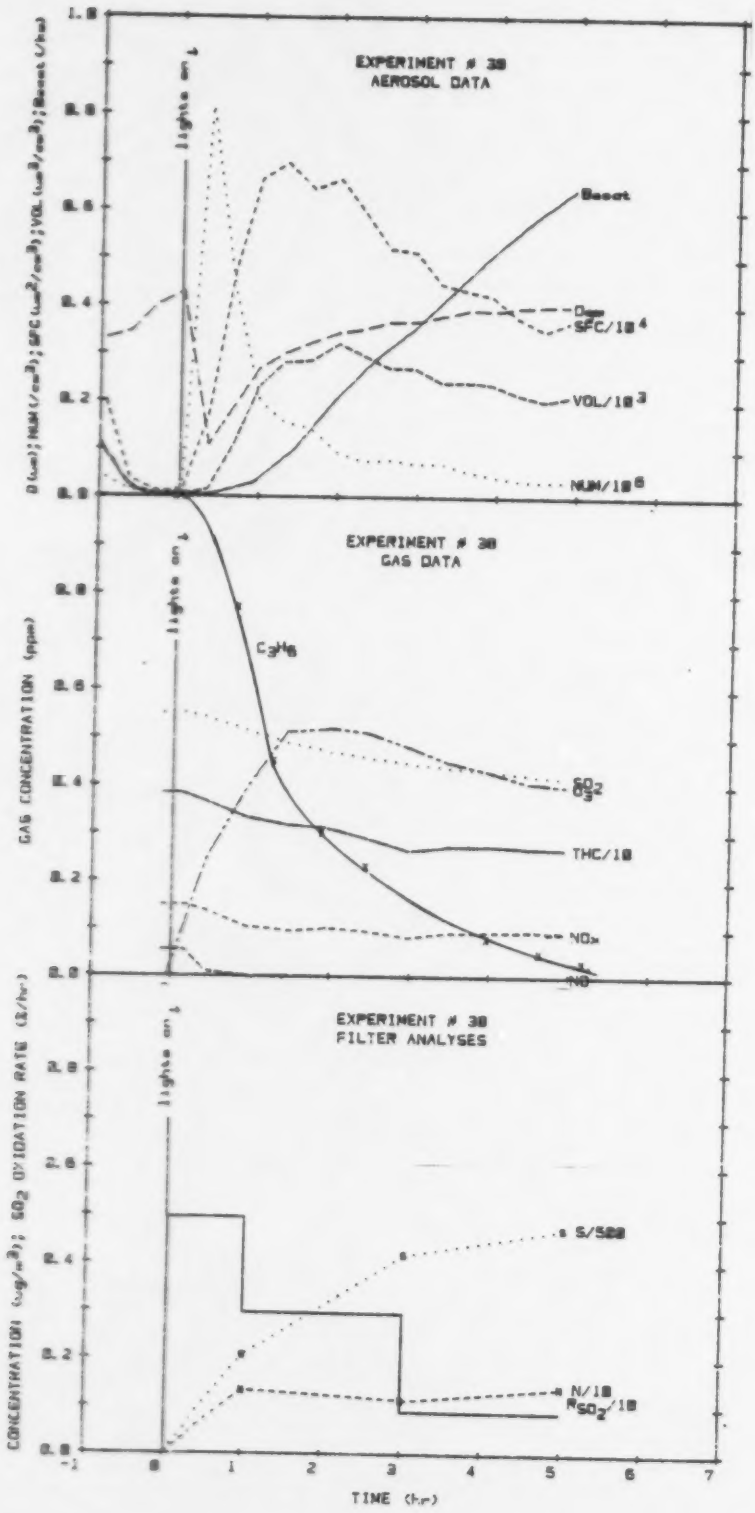

EXPERIMENT # 13
FILTER ANALYSES
DARK REACTION
O/1000
E/5000
N/18
S/100
CONCENTRATION (ug/m³); SO_2 OXIDATION RATE (%/hr)
TIME (hr)

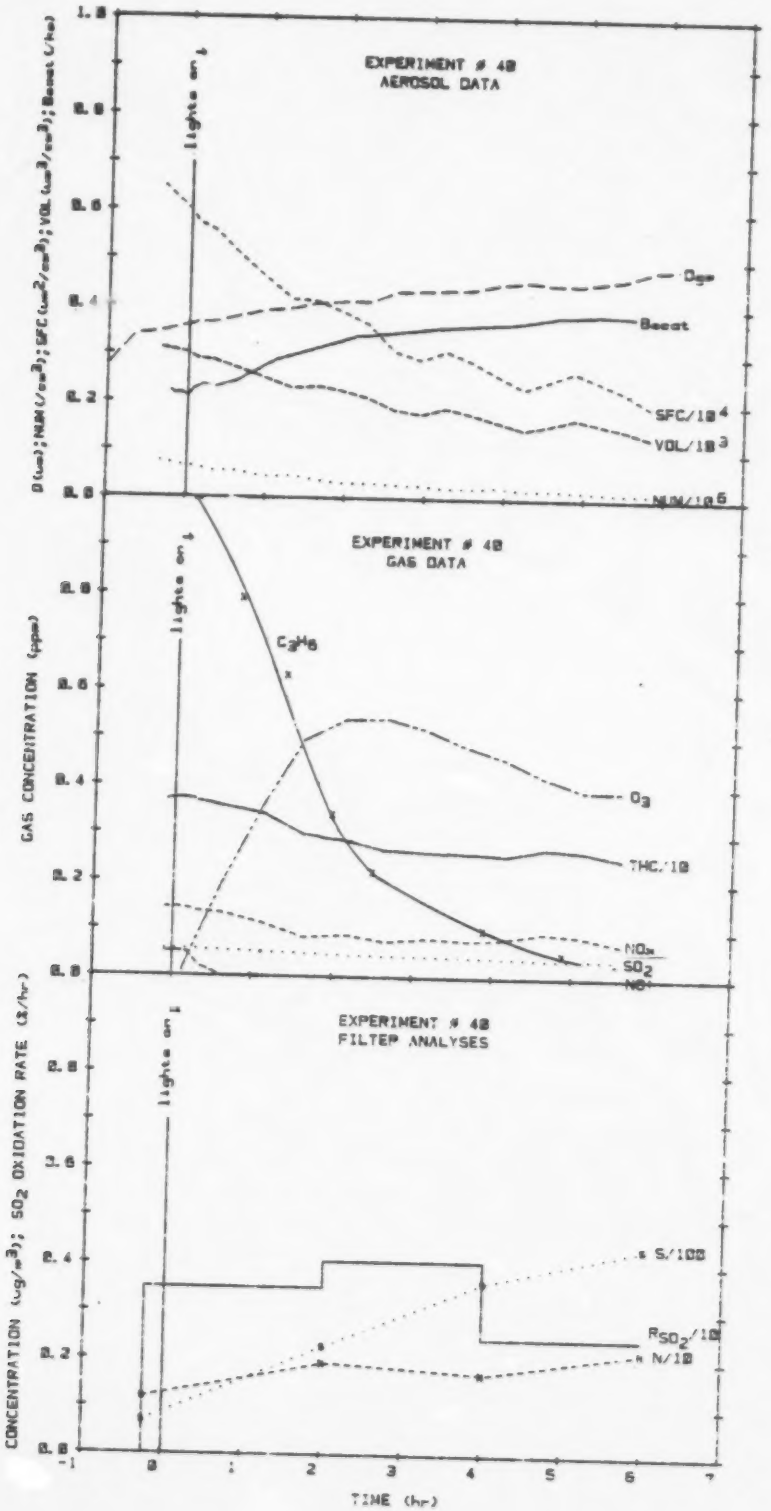

EXPERIMENT # 33
FILTER ANALYSES
DARK REACTION
S/100
N/100
OZONE GENERATOR ON
$R_{SO_2}/1$
CONCENTRATION ($\mu g/m^3$); SO_2 OXIDATION RATE (%/hr)
TIME (hr)
1.0
0.8
0.6
0.4
0.2
0.0
-1
0
1
2
3
4
5
6
7

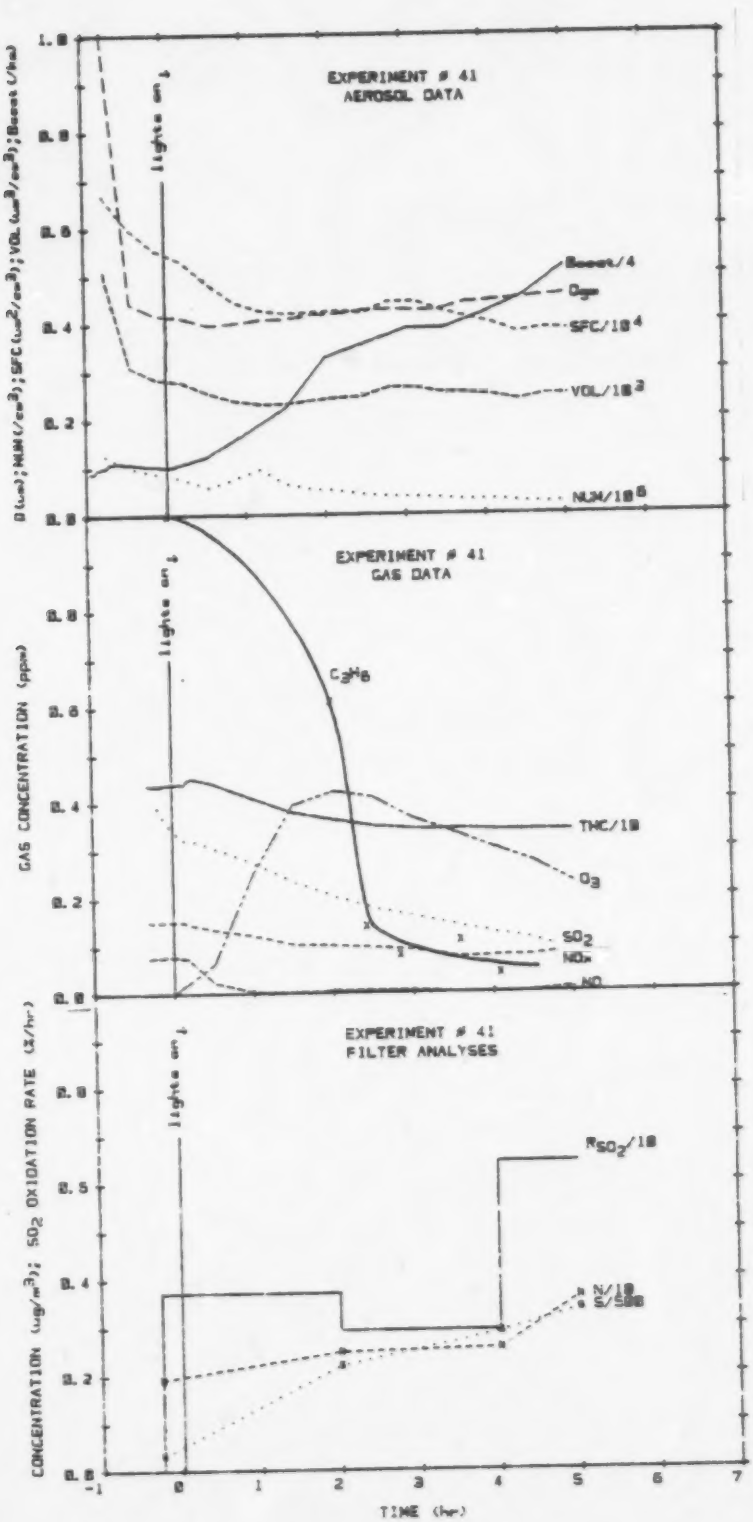

EXPERIMENT # 35
GAS DATA
O_3
SO_2
NO_x
NO
OZONE GENERATOR ON
GAS CONCENTRATION (ppm)
EXPERIMENT # 35
FILTER ANALYSES
DARK REACTION
N/100
S/500
$P_{SO_2}/10$
CONCENTRATION ($\mu g/m^3$); SO_2 OXIDATION RATE (%/hr)
TIME (hr)

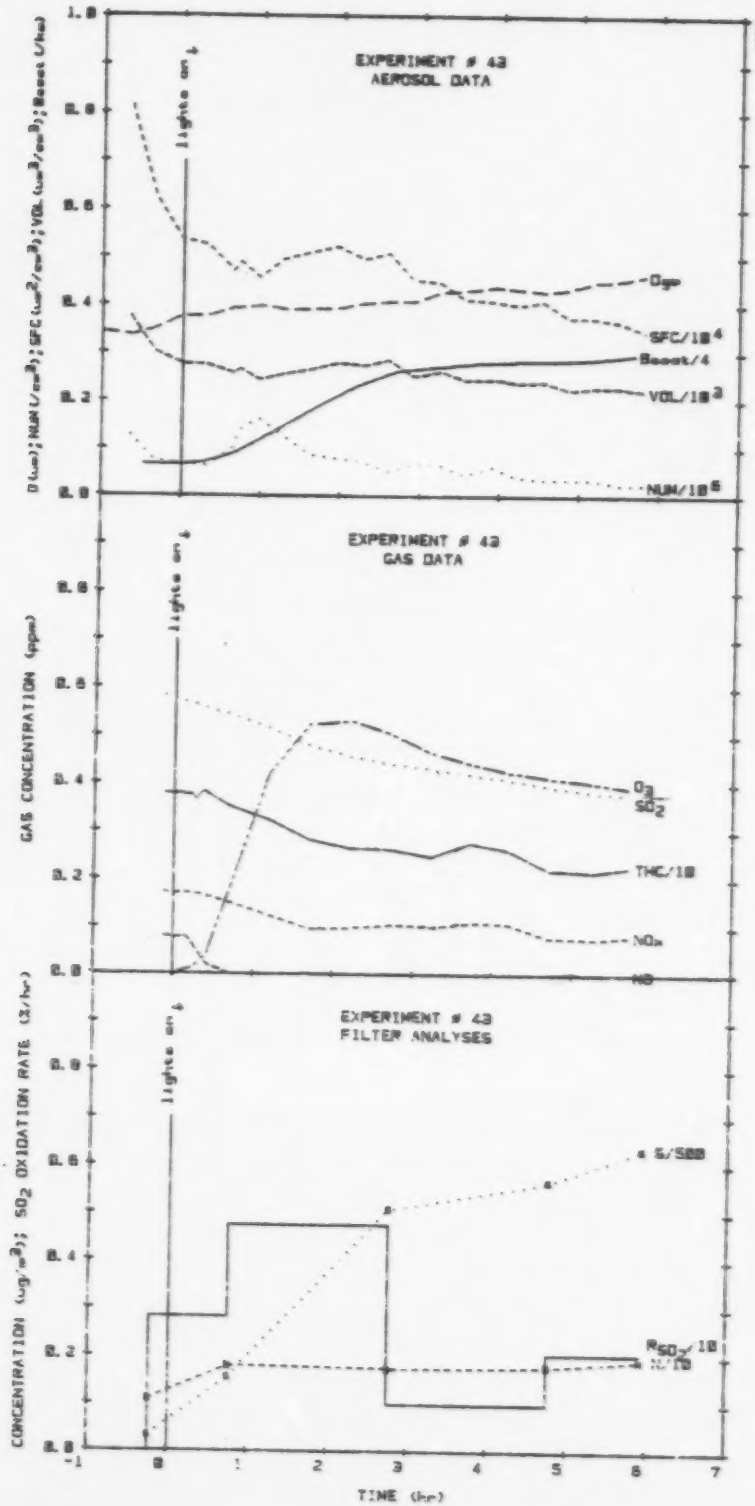

EXPERIMENT # 38
AEROSOL DATA
lights on
Bscat
O_{3p}
SFC/10^4
VOL/10^3
EXPERIMENT # 38
GAS DATA
lights on
GAS CONCENTRATION (ppm)
SO_2
THC/10
NOx
O_3*10
NO
EXPERIMENT # 38
FILTER ANALYSES
lights on
CONCENTRATION (ug/m^3); SO_2 OXIDATION RATE (%/hr)
S/500
N/10
R_{SO_2}/10
TIME (hr)

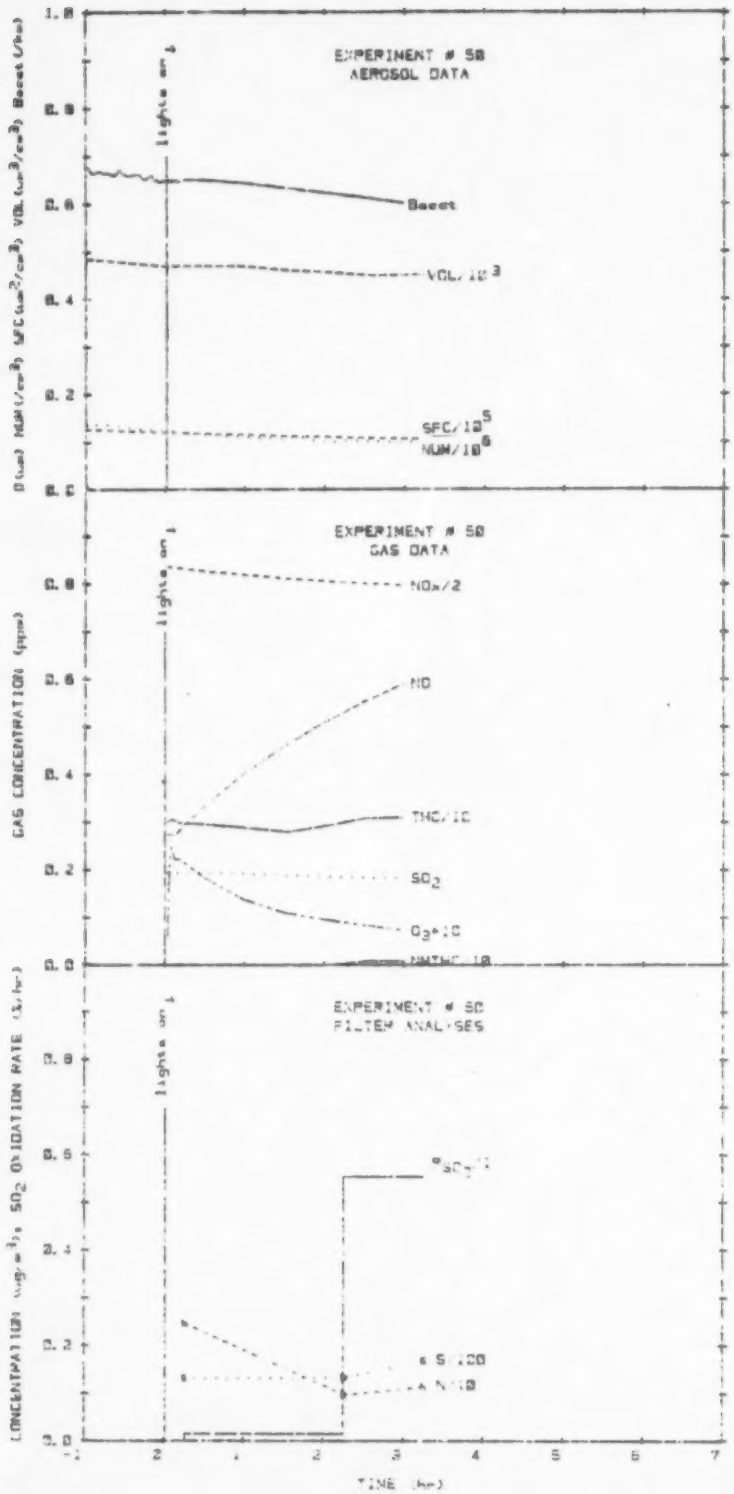

EXPERIMENT # 37
AEROSOL DATA
lights on
Dgn
Bscat/4
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 37
GAS DATA
lights on
SO2
THC/10
O3
NOx
NO
EXPERIMENT # 37
FILTER ANALYSES
lights on
S/500
E/500
R SO2 /10
O3/100
N/10
TIME (hr)

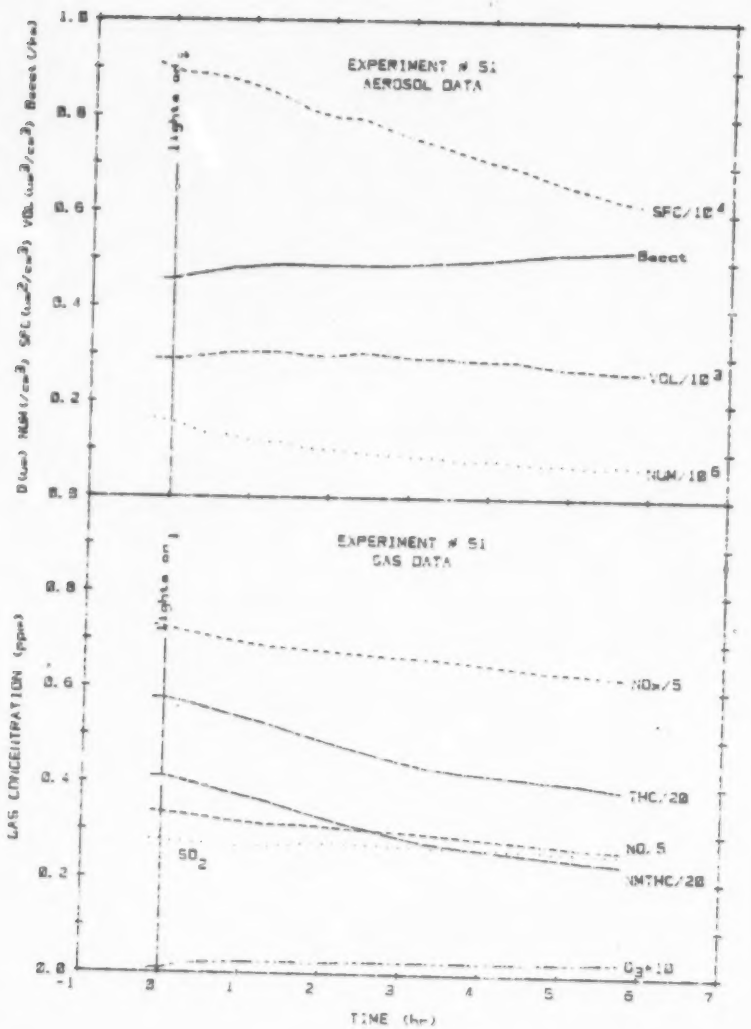

EXPERIMENT # 38
AEROSOL DATA
lights on
Bscat
D_{pm}
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 38
GAS DATA
lights on
C_3H_6
SO_2
O_3
THC/10
NO_x
NO
EXPERIMENT # 38
FILTER ANALYSES
lights on
S/500
N/10
R_{SO_2}/10
TIME (hr)

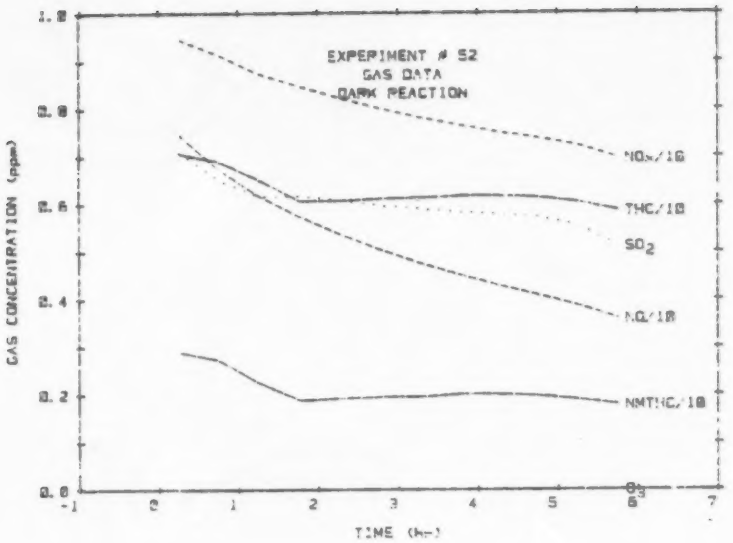

EXPERIMENT # 48
AEROSOL DATA
lights on
Dgn
Bscat
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 48
GAS DATA
lights on
C2H6
O3
THC/10
NOx
SO2
NO
EXPERIMENT # 48
FILTER ANALYSES
lights on
S/100
RSO2/10
N/10
TIME (hr)

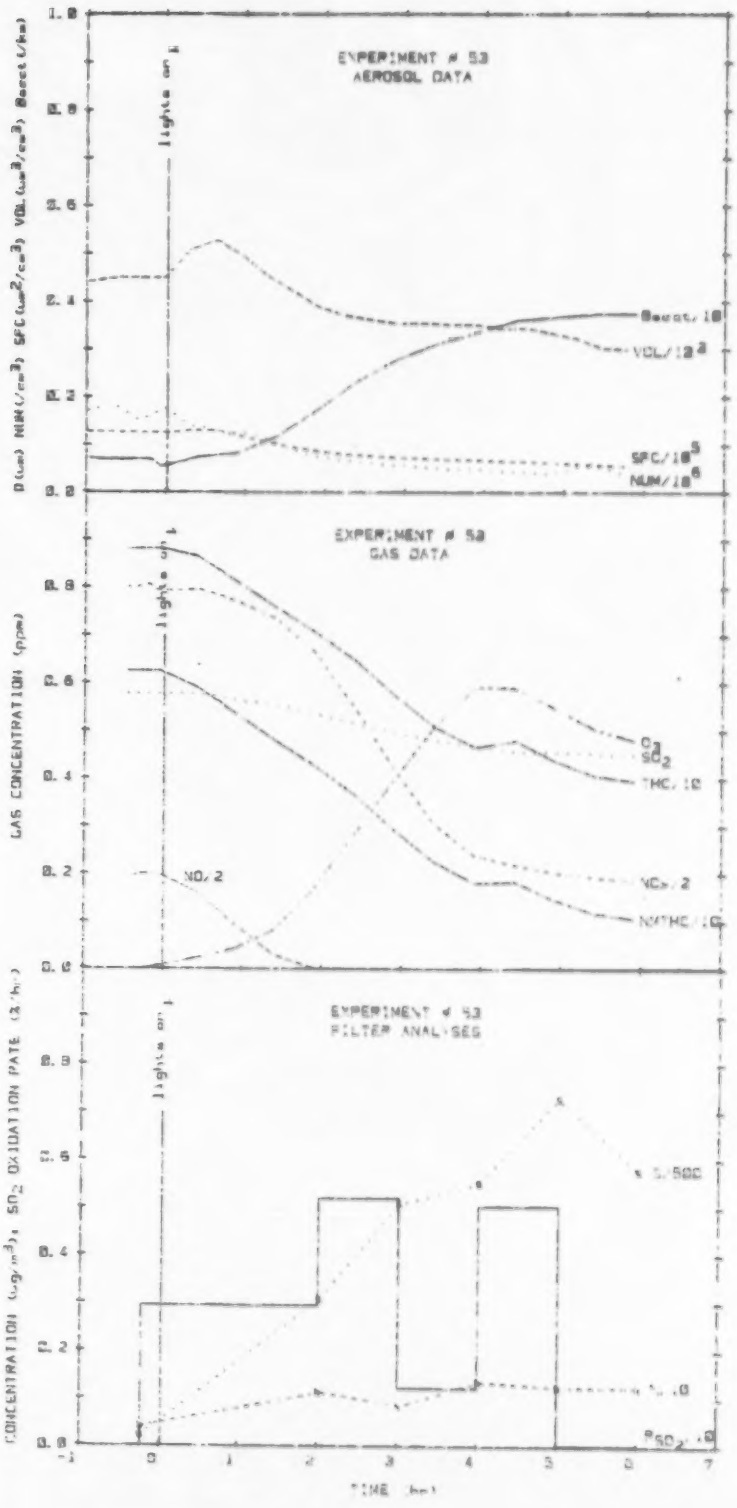

EXPERIMENT # 41
AEROSOL DATA
lights on
Bscat/4
Dgm
SFC/10^4
VOL/10^3
NUM/10^6
EXPERIMENT # 41
GAS DATA
lights on
C3H8
THC/10
O3
SO2
NOx
NO
EXPERIMENT # 41
FILTER ANALYSES
lights on
RSO2/10
N/10
S/500
TIME (hr)

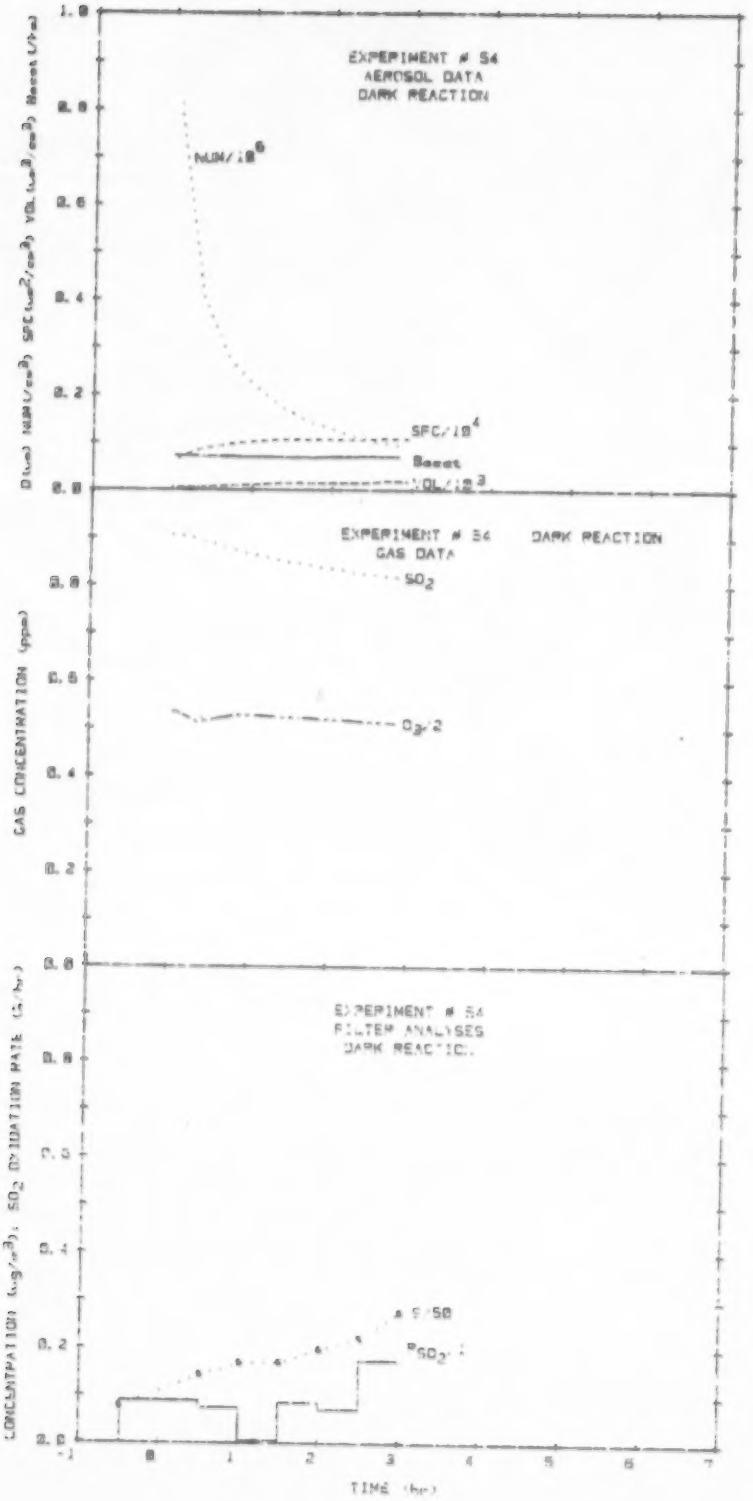

EXPERIMENT # 43
AEROSOL DATA
lights on
Dgp
SFC/10^4
Boost/4
VOL/10^2
NUM/10^6
EXPERIMENT # 43
GAS DATA
lights on
GAS CONCENTRATION (ppm)
O3
SO2
THC/10
NOx
NO
EXPERIMENT # 43
FILTER ANALYSES
lights on
CONCENTRATION
SO2 OXIDATION RATE
4 S/SBB
RSO4/10
TIME (hr)

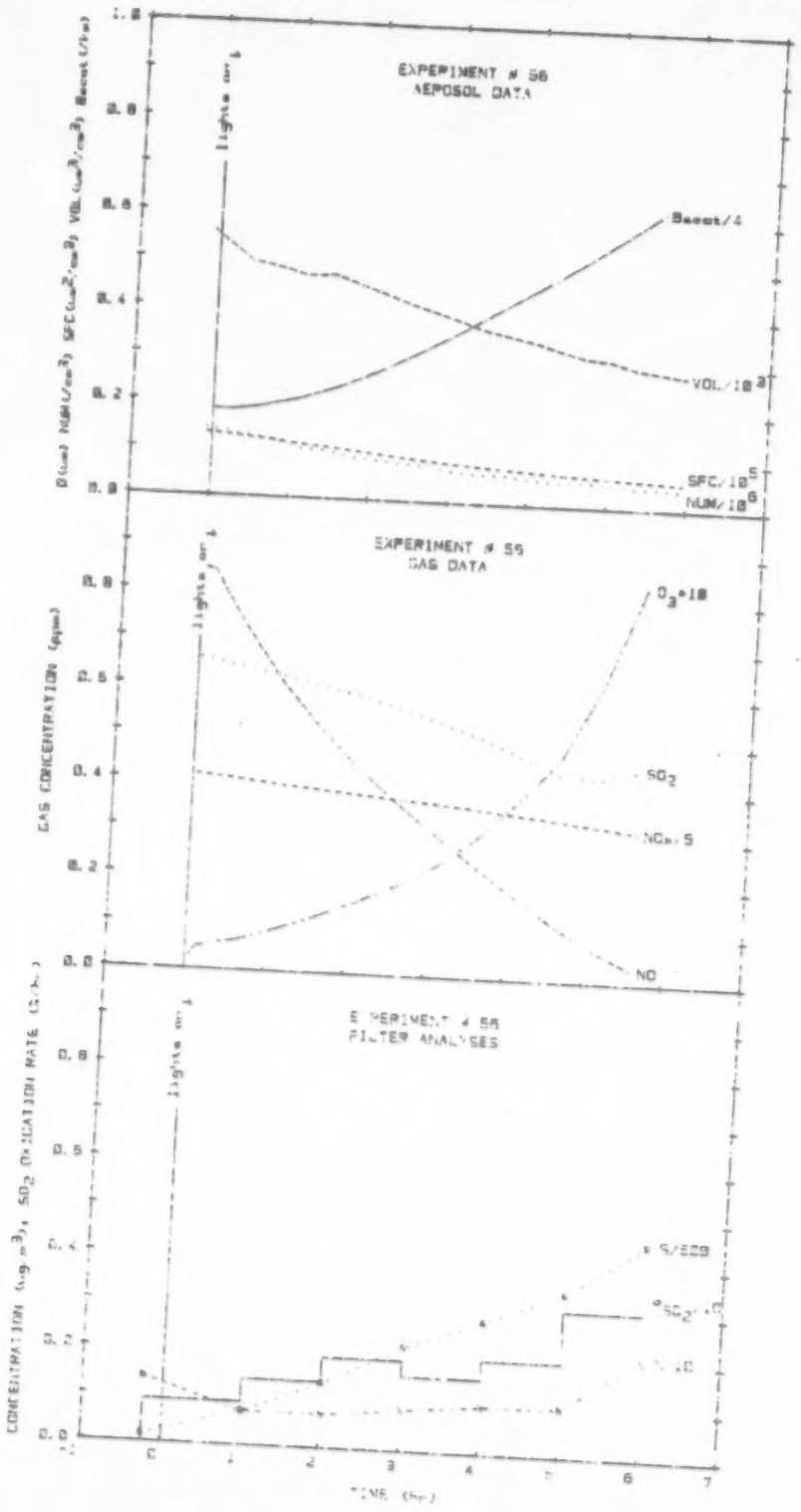

EXPERIMENT # 58
AEROSOL DATA
lights on
Bscat
VOL/10^3
SFC/10^5
NUM/10^6
EXPERIMENT # 58
GAS DATA
lights on
NOx/2
NO
THC/10
SO2
O3*10
EXPERIMENT # 58
FILTER ANALYSES
lights on
TIME (hr)

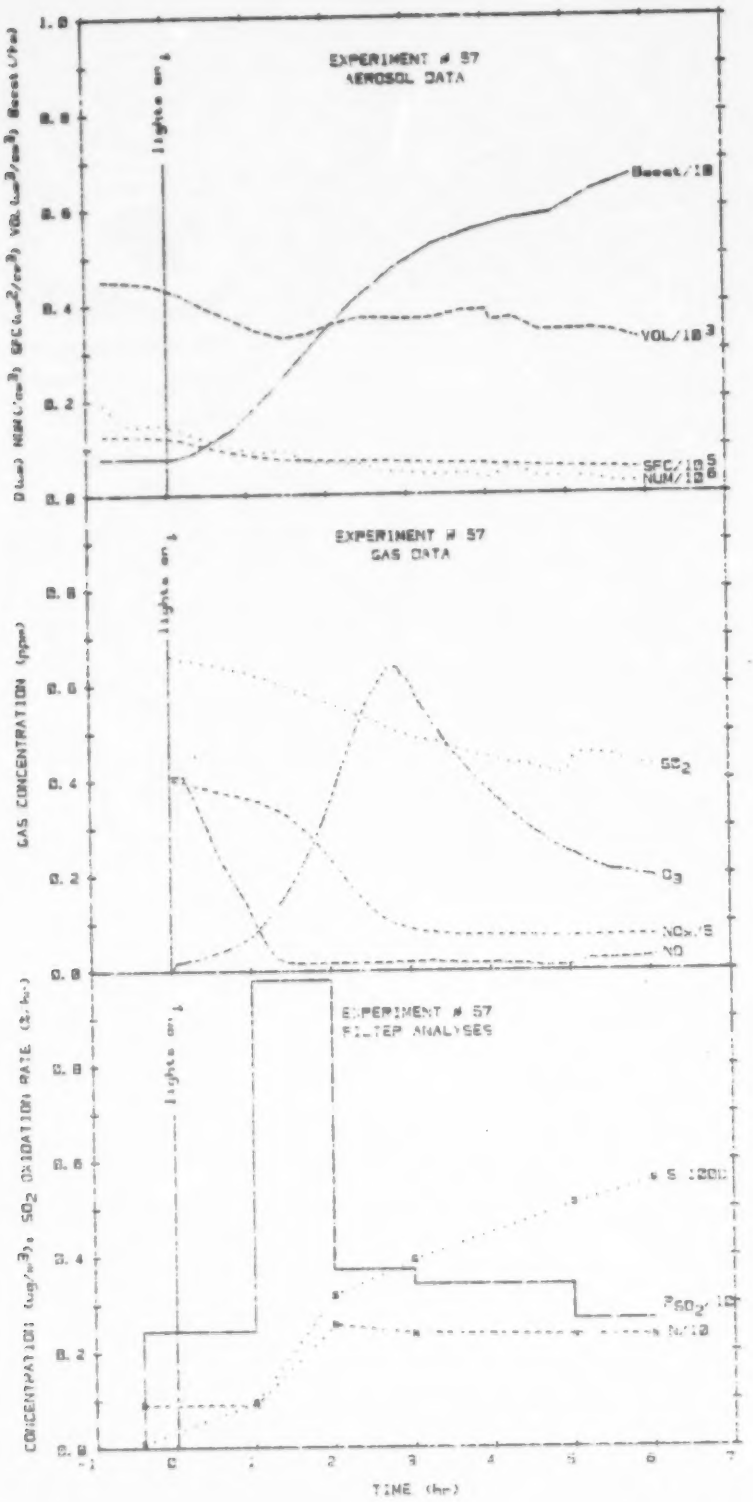

EXPERIMENT # S1
AEROSOL DATA
lights on
SFC/10^4
Bscat
VOL/10^3
NUM/10^6
EXPERIMENT # S1
GAS DATA
lights on
NOx/5
THC/20
NO. 5
NMTHC/20
SO2
O3*10
GAS CONCENTRATION (ppm)
TIME (hr)

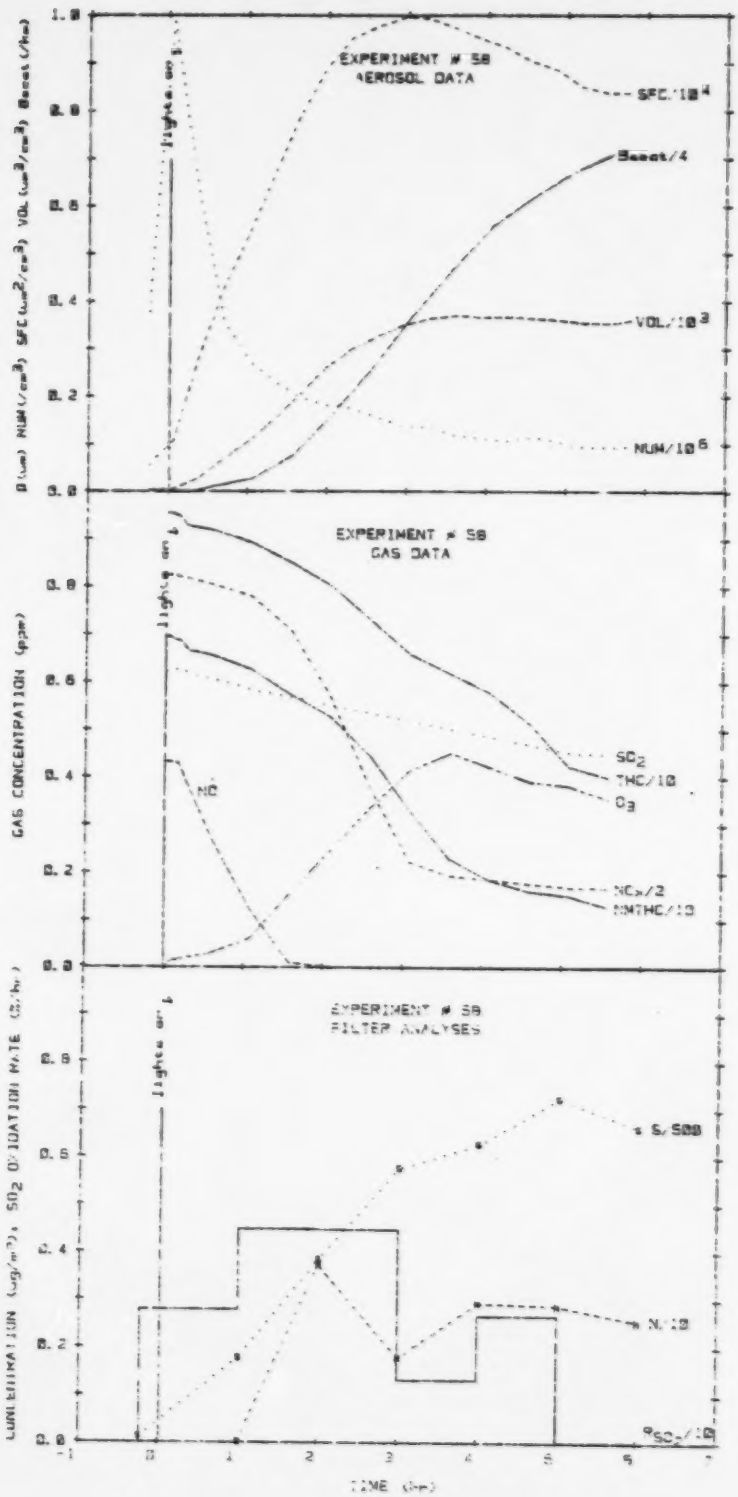

EXPERIMENT # 52
GAS DATA
DARK REACTION
NOx/10
THC/10
SO2
NO/10
NMTHC/10
O3
GAS CONCENTRATION (ppm)
TIME (hr)
1.0
0.8
0.6
0.4
0.2
0.0
-1
0
1
2
3
4
5
6
7

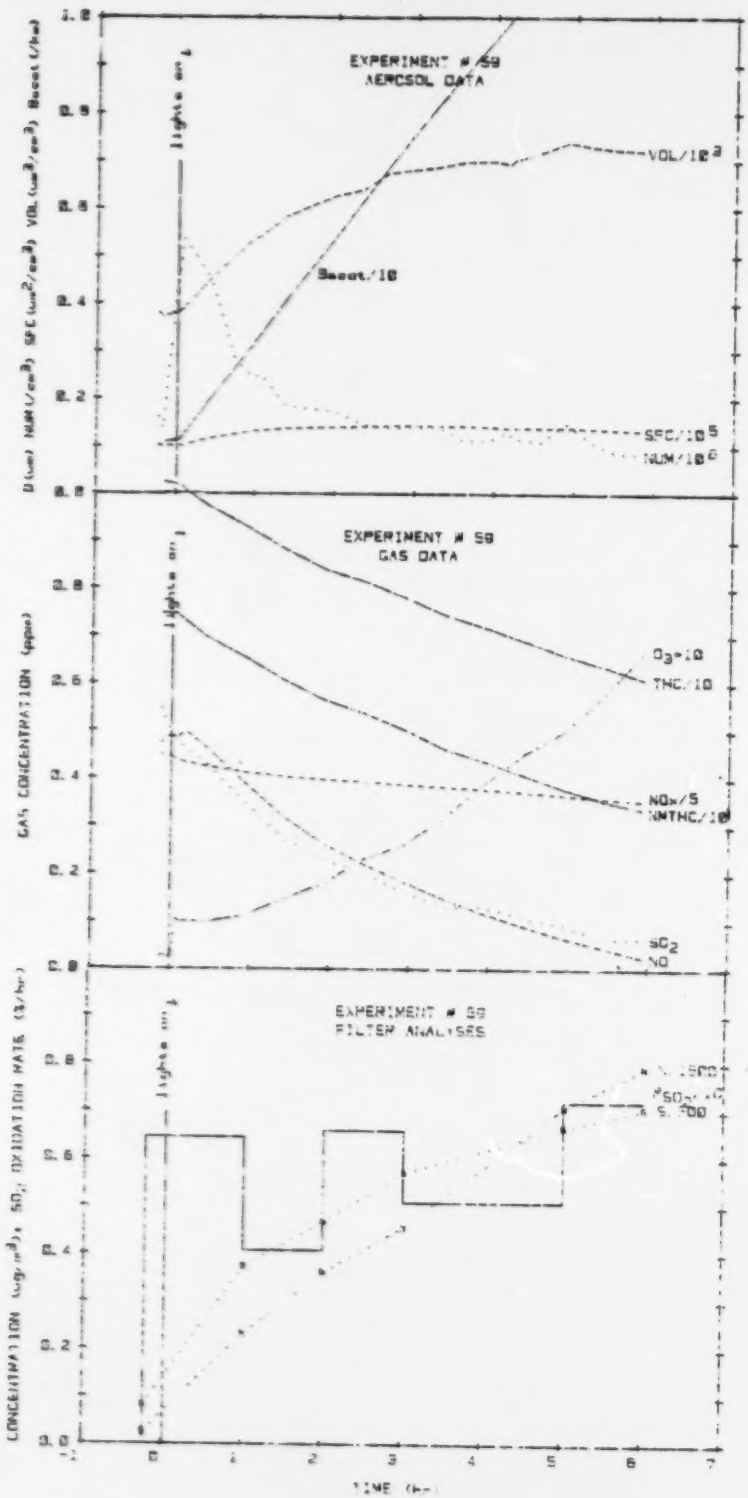

EXPERIMENT # 53
AEROSOL DATA
lights on
Dscat/10
VOL/10^2
SPC/10^5
NUM/10^6
EXPERIMENT # 53
GAS DATA
lights on
O3
SO2
THC/10
NO/2
NOTHC/10
EXPERIMENT # 53
FILTER ANALYSES
lights on
TIME (hr)

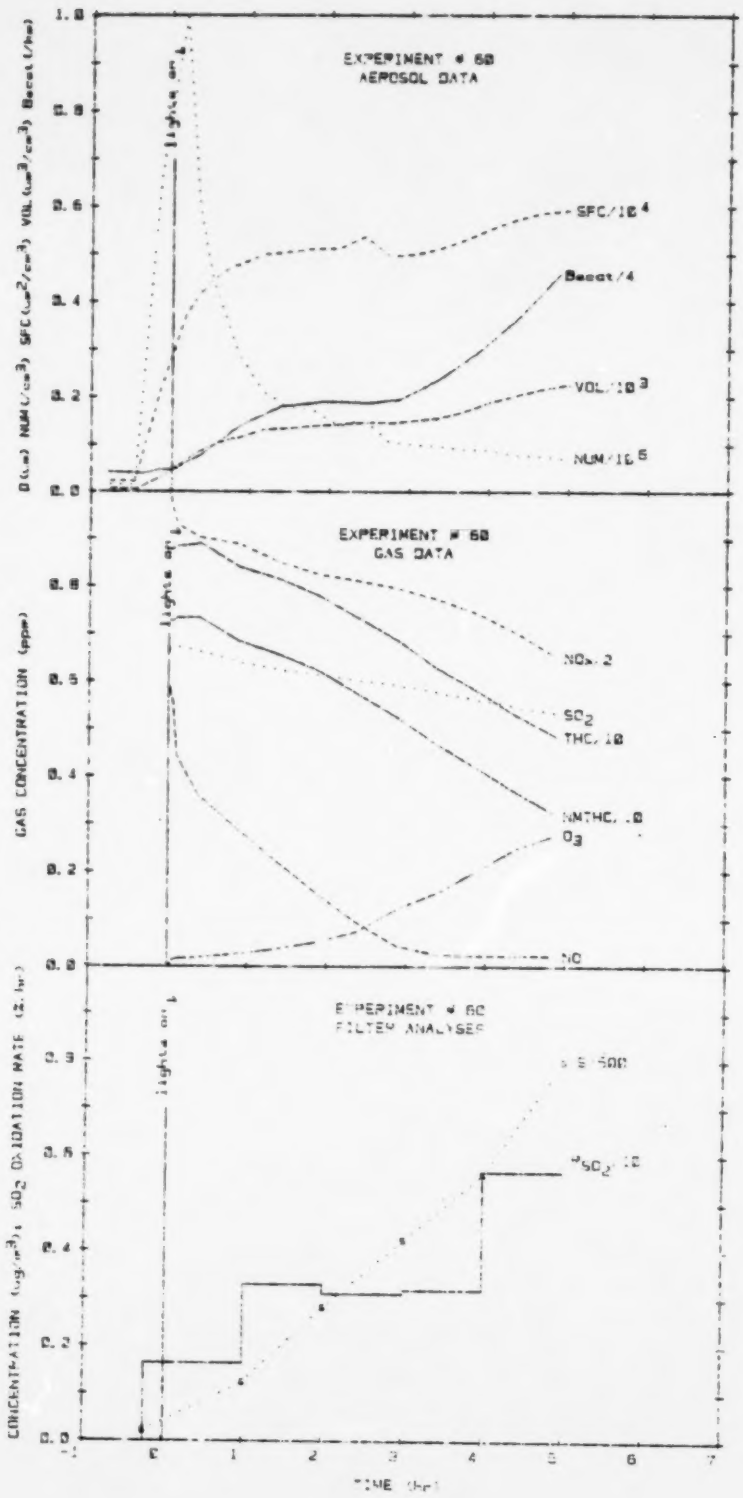

EXPERIMENT # 54
AEROSOL DATA
DARK REACTION
NUM/10^6
SFC/10^4
Bscat
VOL/10^3
EXPERIMENT # 54
GAS DATA
DARK REACTION
SO2
O3/2
EXPERIMENT # 54
FILTER ANALYSES
DARK REACTION
TIME (hr)


EXPERIMENT # 56
AEROSOL DATA
lights on
Bscat/4
VOL./10^3
SFC./10^5
NUM/10^6
EXPERIMENT # 56
GAS DATA
lights on
O3*10
SO2
NOx/5
NO
EXPERIMENT # 56
FILTER ANALYSES
lights on
TIME (hr)


EXPERIMENT # 57
AEROSOL DATA
lights on
Bscat/18
VOL/18^3
SFC/18
NUM/18
EXPERIMENT # 57
GAS DATA
lights on
GAS CONCENTRATION (ppm)
SO2
O3
NOx/5
NO
EXPERIMENT # 57
FILTER ANALYSES
lights on
S (20)
FSO2' 10
N/10
TIME (hr)


EXPERIMENT # 58
AEROSOL DATA
SFC/10^4
Beext/4
VOL/10^3
NUM/10^6
EXPERIMENT # 58
GAS DATA
SO2
THC/10
O3
NO
NOx/2
NMTHC/10
EXPERIMENT # 58
FILTER ANALYSES
TIME (hr)


EXPERIMENT # 59
AEROSOL DATA
Lights on
VOL/10^2
Bscat/10
SPC/10^5
NUM/10^6
EXPERIMENT # 59
GAS DATA
Lights on
O3*10
THC/10
NOx/5
NMTHC/10
SO2
NO
EXPERIMENT # 59
FILTER ANALYSES
Lights on
TIME (hr)


EXPERIMENT # 60
AEROSOL DATA
Lights on
SFC/10^4
Bscat/4
VOL/10^3
NUM/10^5
EXPERIMENT # 60
GAS DATA
Lights on
NO2 x 2
SO2
THC/10
NMTHC/10
O3
NO
EXPERIMENT # 60
FILTER ANALYSES
Lights on
TIME (hr)

Appendix B
Aerosol Mass Loading

Aerosol mass loadings measured at the end of the indicated experiments are presented in Table 4. The aerosol mass loadings (in units of $\mu g/m^3$) were determined by at least one of three possible methods based on: aerosol size characterization from EAA (electrical mobility) and Royco (optical) aerosol analyzers; chemical analyses to obtain individual masses of composite aerosol samples; and gravimetric-analyses of high volume samples. These approaches, and their inherent uncertainties, are discussed below.

Filter samples were chemically analyzed to determine the mass of $SO_4^=$, NO_3^-, elemental carbon and organic carbons present in the chamber. Due to the hygroscopicity of H_2SO_4, $SO_4^=$ was assumed to be in the form of hydrated H_2SO_4 in the chamber. Using published tables (Bray, 1970), the equilibrium mass of hydrated H_2SO_4 was determined from the measured mass of $SO_4^=$ and the chamber relative humidity at the time the sample was obtained. The sum of the mass of hydrated H_2SO_4, NO_3^-, and elemental and organic carbon yielded the mass loading determined by chemical analysis. All other species were ignored.

The aerosol analyzers provided a measure of the aerosol volume in the chamber. Based on the chemical analysis data and the relative humidity, an average density of an individual composite aerosol particle was computed. This value is recorded in Table 4 as the calculated density (g/cm^3). When chemical analyses were unavailable, the aerosol density was assumed equal to the average of the calculated densities ($1.7\ g/cm^3$) for which chemical analyses were available. The product of the aerosol volume and average density yielded the mass loading by aerosol analyzers.

For high volume samples, the mass of the sampled aerosol was determined by the difference in filter weight before and after sampling. From this, and knowledge of the sampling rate ($\sim 10\ m^3/min$), the mass loading was calculated.

Table 4
AEROSOL MASS LOADING

EXPERIMENT	RH (%)	CALCULATED DENSITY (g/cm^3)	MASS LOADING ($\mu g/m^3$) DETERMINED BY:		
			AEROSOL ANALYZERS	CHEMICAL ANALYSIS	HI-VOL SAMPLES
1	68	–	–	–	1750
2	62	–	–	–	1750
3	71	2.1	–	3980	1750
4	59	–	–	–	1850
6	45	1.7*	140	–	–
12	48	1.4	20	110	60
13	91	2.2	–	3490	1420
14	53	2.2	290	200	140
15	86	2.1	–	2660	1420
16	50	1.9	400	340	250
17	28	1.6	100	270	–
18	14	1.7	180	350	370
19	24	1.6	580	700	820
21	13	1.5	430	260	740
22	21	1.6	400	690	990
23	51	1.9	380	240	230
24	46	1.7	340	330	290
25	21	1.5	170	500	640
26	20	1.7*	200	–	600
28	14	1.4	160	320	620
29	29	1.4	90	300	390
30	97	–	–	–	2000
33	73	–	–	–	740
34	67	–	–	–	1430
36	29	1.7*	170	–	300
37	33	1.7*	160	–	810
38	37	1.7*	360	–	–
40	43	1.7*	220	–	250
41	71	1.7*	420	–	–
43	45	1.7*	370	–	510
44	44	–	–	–	1840

*ASSUMED VALUE

Each of these methods of computing the aerosol mass loading has inherent uncertainties which need to be considered. Mass loading computed from chemical analysis assumes that the aerosol is composed entirely of sulfates, nitrates, elemental carbon and organic carbons. XRF analyses of selected samples confirmed that concentrations of other elements and compounds were not significant. Potential errors in determination of mass as well as the measured volumetric distribution of the aerosol. Aerosol size characterization devices provide diameter versus concentration data which must be cubed to produce volumetric data, greatly increasing uncertainties associated with the aerosol size characterizations. Determinations of density of the aerosol are based upon the results of chemical analyses and the assumption of an average density for the organic carbon compounds (1.2 g/cm^3). Hence, uncertainties in the chemical analyses of the aerosol samples are carried over to density determinations.

The high volume samples provided the most direct means of computing the aerosol mass loading. However, due to both filter loading and the recirculatory nature of the sampling system, the volume of the chamber sampled is uncertain. Considering these aspects, an appropriate sample volume was assumed (360 and 300 m^3 for experiments #1-30 and 31-60, respectively).

Of the three techniques, it is our judgement that the chemical analysis approach provides the most confident measure of relative change in aerosol mass loading. Considering the uncertainties involved, the agreement between the mass loadings calculated from the different approaches is quite good.

Appendix C
EXPERIMENTAL APPARATUS AND PROCEDURE

The tests were performed in Calspan's 600 m^3 indoor smog chamber. Systems under investigation were composed of diluted diesel exhaust and artificially high values of SO_2 and reactive hydrocarbons. The exhaust emissions were generated by one of two diesel-fueled automobiles and one gasoline-fueled automobile, mounted upon a chasis dynamometer, and manually operated through a programmed driving cycle. Depending upon the experimental plan, before reaching the chamber the exhaust could be modified by: a) partial filtration of particulates using a hot-emissions tail pipe filter; and/or b) dilution via passage through a constant volume sampler. Once in the chamber, the exhaust could be further modified by: a) additional dilution; b) additional filtration; or, c) the addition of gases (e.g., hydrocarbons, SO_2, O_3, etc). This final system was then subjected to specific conditions for the desired time period. Gas and aerosol analyzers continuously monitored the chamber environment providing data on the gas and aerosol reactions. Filter samples for sulfate, nitrate and carbon were taken periodically during the experiment. At the conclusion of many experiments, high volume samples for mutagenic testing were obtained.

DIESEL EMISSIONS

Two light-duty diesel vehicles served as sources of the required diesel emissions during this program: a 1978 Mercedes 240D, leased locally, and a 1975 Nissan-Datsun, supplied by EPA. The Mercedes was a new vehicle with less than 10,000 miles. Tests performed by USEPA-Ann Arbor provided the following Federal Test Procedure emissions data for the Mercedes (units are g/km):

HC (HFID)	0.07
CO	0.55
CO_2	208
NO_x	1.0
Particulates	0.27

The Nissan-Datsun had been tested extensively by EPA and registered in excess of 25,000 miles. The fuel used in these tests was a #2D diesel supplied by EPA. It was a 32.5% aromatic fuel with an API gravity of 35.5 containing 0.16% sulfur. A 3.8 liter 1980 Buick Regal (V-6) supplied the necessary gasoline-fueled, catalyst-equipped emissions during the latter phase of the program. The Buick was also a new vehicle and registered about 1000 miles. The unleaded fuel required for those tests was purchased commercially from a large stock.

A Clayton CT-50 chassis dynamometer was used to simulate the drag and inertial forces of driving. Vehicle inertia effects, experienced during acceleration and deceleration driving modes, were simulated with manually adjustable inertia flywheels. Vehicle rolling losses and aerodynamic drag were simulated with a water-cooled, power-absorption unit that has a maximum rating of 50 hp.

Two driving cycles were used during the program. The first four tests used the Urban Driving Cycle simulating stop-and-go city driving. The remainder of the tests used the Fuel Economy Test driving cycle simulating highway conditions. Both driving cycles are described in the Federal Register. The autos were tested under 'hot' engine conditions produced by a 30-minute operation on the dynamometer at highway speeds. Following a subsequent 10-minute shut-down interval, the engine was started and the driving cycle commenced.

In most of the experiments, it was necessary to dilute the emissions to produce aerosol mass loadings more representative of urban areas as well as to reduce aerosol concentrations to allow in-situ monitoring by aerosol characterization devices. With regard to simulating urban atmospheres, gases (reactive hydrocarbons, SO_2, and O_3) were added to the emissions. Gas sampling cells containing known quantities of SO_2 or HC were flushed with dry nitrogen to introduce these gases into the chamber. The introduction of precise

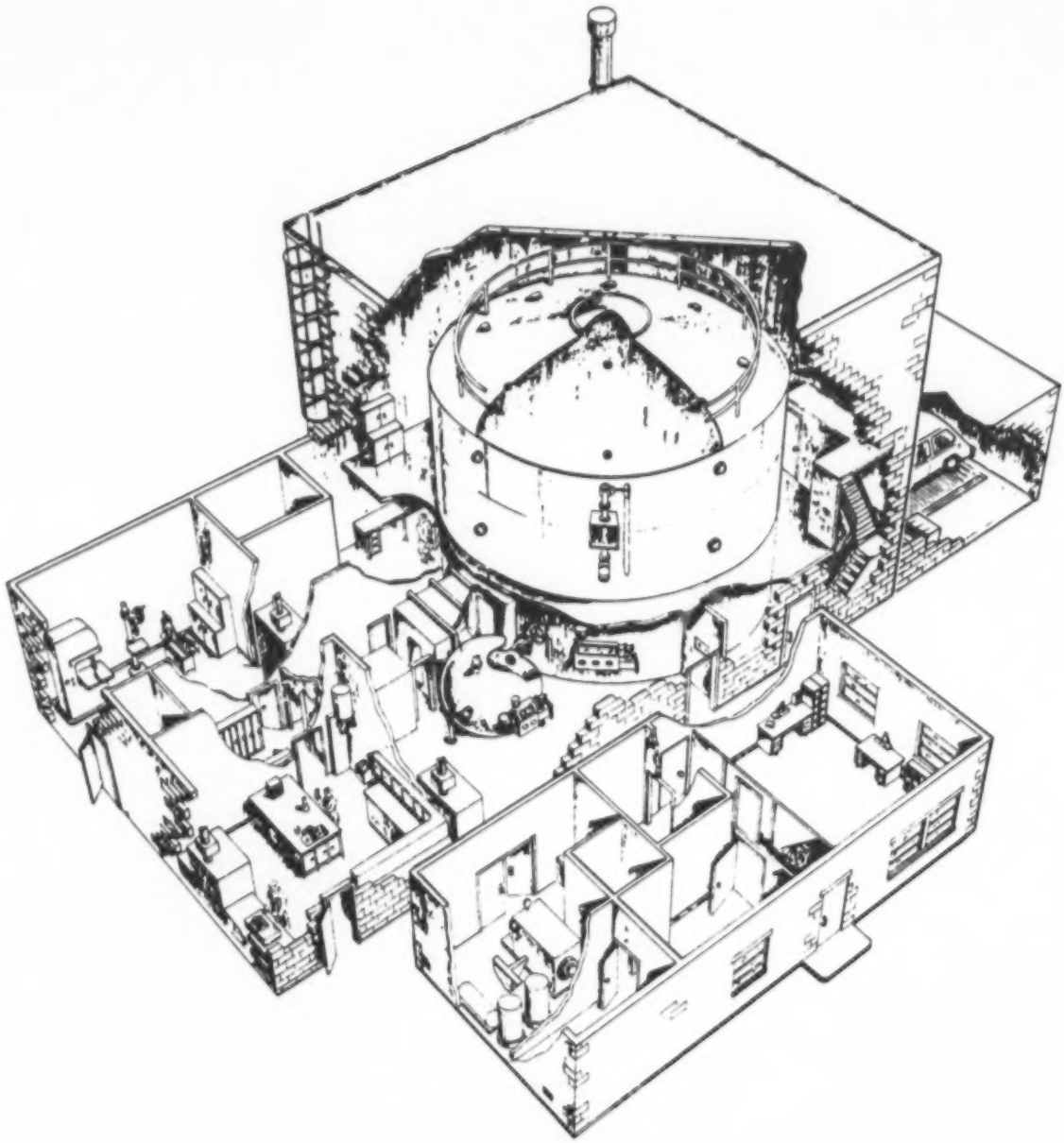
quantities of such gases into the known volume of the chamber also served to produce a source of span gas for the SO_2 and HC analyzers. O_3 was introduced into the chamber from an Orec ozonator at a rate determined from the output curves provided by the manufacturer. Ultimate control of the O_3 concentration was based upon measurements by the O_3 monitor. In some tests, the primary particulates of the diesel emissions were eliminated to study their influence on the evolution of the system.

Diesel emissions were modified by a variety of methods. Modification of the emissions prior to their introduction into the chamber consisted of dilution by a constant volume sampler and/or filtration of the emissions at the exhaust of the auto. In-line filtration of the emissions was achieved with a large surface area, low pressure drop filter provided by EPA. The filter was effective in removing >90% of the primary particulates of the diesel emissions.

Dilution of emissions before their introduction into the chamber was provided by an Olson Constant Volume Sampler (CVS) Model 45E-R3. Vehicle exhaust gases were routed through about 6 feet of flexible, leakproof, stainless-steel tubing (3 inch I.D.) to the variable dilution CVS, where they were diluted with filtered, ambient air. Within the CVS, the exhaust gases and the diluent gas were thoroughly mixed in a mixing chamber and drawn through a heat exchanger with a positive-displacement, four-speed air pump. Operated at a constant speed and with the gas maintained at a known fixed temperature, the CVS maintained a constant volumetric flow rate. Volumetric flow rates of 150, 225, 300 and 400 CFM were available. An auxiliary positive displacement pump was used to draw a fraction of the diluted emissions from the CVS for injection into the chamber. The unused portion of the diluted emissions was discharged into the atmosphere.

Once in the chamber, the emissions could also be diluted with absolute filtered air or recirculated through absolute filters to remove the primary particulates. These and other features of the smog chamber are discussed below. With the exception of O_3, any gases to be added to the emissions were introduced into the chamber after dilution and filtration of the diesel emissions had been completed. The introduction of known quantities of gases into the chamber was accomplished volumetrically or by metering. In the

Figure 7. Cut-away view of Calspan Environmental Simulation Facility



final group of experiments (#37-60), approximately 0.5 ppm O_3 was added to the chamber prior to the introduction of the diluted emissions. The presence of O_3 in the chamber served to deactivate the chamber walls (i.e., eliminate dark reactions) and to decrease the NO/NO_x ratio (i.e., decrease the time required for the formation of the O_3 peak).

Chamber

The Calspan smog chamber has been described in substantial detail elsewhere (e.g., Kocmond et al, 1973) and will only briefly be reviewed here. The facility itself consists of a cylindrical chamber 9.14 meters (30 feet) in diameter and 9.14 meters (30 feet) high enclosing a volume of 600 m^3 (20,800 ft^3). A cut-away view of the entire facility is illustrated in Figure 7. The 1.25 cm thick steel wall of the chamber is designed to withstand pressure differentials of 60 kilopascals (6.1 m of water); however, the Pyrex cover plates of the irradiation system currently limit pressure differentials to about 3.9 kilopascals (40 cm of water). The inner chamber surface is coated with a fluoroepoxy-type urethane (developed at the Naval Research Laboratory, Washington, DC) which has surface energy and reactivity properties comparable to those of FEP Teflon. Illumination within the chamber is provided by 28.6 kw of fluorescent blacklight and sun lamps installed inside 24 lighting modules and arranged in eight vertical channels attached to the wall of the chamber. Each lighting module contains two 40-watt sun lamps, eight 85-watt high output black lamps, and two 215-watt specially-produced black lamps. The lighting modules are covered with 0.5 cm thick Pyrex glass and are air cooled and sealed from the chamber working volume in order to minimize sources of contamination inside the chamber.

Measured light intensity using the k_d $[NO_2]$ method reported by Stedman & Niki (1973) was $k_d \sim 0.24$ min^{-1} for experiments #1 through 30. Because this intensity was lower than desired, due to aging of the lamps, all of the lamps of the irradiation system were replaced after experiment #30. Following an initial "burn-in" period, a new k_d of ~ 0.52 min^{-1} was measured.

The air circulation system of the chamber allows for both filtration and dilution of the chamber environment. Large absolute filters (Cambridge Absolute Filter Model 1ET-1000) typically reduced Aitken particle concentration to less than 1000 cm^{-3} in less than an hour of filtration. By flushing

the chamber with filtered fresh air, the chamber could be diluted by a factor of 2 in about 10 minutes. A series of activated carbon filters was also available for gas filtration, though these were not necessary for this project.

Chamber washdown and humidification systems were in frequent use during this program's tests. The recirculating washdown system consists of a stainless steel spray head which rotates on two axes and can wet all of the chamber surfaces with distilled water or cleaning solution. Generally, the procedure was to first wash the chamber surfaces with a 5% solution of a laboratory glass cleaning agent followed by two or three rinsings with tap water and two final rinsings with distilled water. Drying was accomplished by fresh air flushing followed by air filtration. Chamber humidity was increased by spraying distilled water into the chamber from a remotely-operated spray nozzle near the chamber top. Chamber dehumidification, when needed, was accomplished by passing the chamber air over refrigeration coils to remove excess water. The system, designed and fabricated at Calspan, is capable of controlling humidity down to about 20% RH.

Instrumentation

Instrumentation used to monitor aerosol behavior and reactant concentrations within the chamber includes a Bendix Model 8002 chemiluminescent ozone analyzer, Model 8101-B nitrogen oxides analyzer, Model 8300 total sulfur analyzer, and the Model 8201 reactive hydrocarbon analyzer, a Thermo Systems Model 3030 Electrical Aerosol Analyzer (EAA), a Model 1550 MRI Integrating Nephelometer, a Gardner Associates small particle detector, a Royco Model 225 Optical Particle Counter, and two Hewlett Packard 5700 gas chromatographs used to monitor low molecular weight hydrocarbons (i.e., propylene and butane). A Meloy flame photometric total sulfur analyzer and an Orec ozonator, both on loan from the EPA, were also used for these experiments.

Each instrument was calibrated daily prior to experiments. The calibration of many of the instruments relied upon internal standards (i.e., O_3 monitor, EAA, Royco, and nephelometer). Known concentrations of specific gases were supplied to calibrate the remainder of the gas analyzers (i.e., SO_2, NO_x and HC) by dilution of span gases with a Thermal Electron Corporation

dilution system. As a verification of the calibration of the SO_2 and HC analyzers, the introduction of specific quantities of SO_2 and HC into the known volume of the chamber provided a very precise source of span gas. Based upon the manufacturers specifications and daily calibrations, the measurements of concentrations of gaseous parameters should have been accurate to within 5%. Measurements of B_{scat} by the integrating nephelometer are expected to have an uncertainty of less than 10%. Potential discrepancies between EAA and Royco determinations of the aerosol size distributions in their common range are discussed in Section 5 under the subsection entitled Aerosol Growth.

Aerosol Sampling and Chemical Analyses

Filter samples were obtained at regular intervals throughout each experiment and subsequently analyzed for their sulfate, nitrate and carbon content. These samples were typically obtained at one-hour intervals and were of 15 minute duration at a sampling rate of about 60 lpm. Sulfate and nitrate concentrations were determined by both ion chromatography and wavelength dispersive x-ray fluorescence. These analytical services were provided by Northrup personnel located at Research Triangle Park, NC. Their support is gratefully acknowledged. Organic and elemental carbons were separated by a pyrolytic technique. Subsequently, each was converted to CH_4 whose concentration was measured by a flame ionization detector. Carbon analyses were performed by Dr. Jim Huntzicker of the Oregon Graduate Center (Johnson et al, 1979). The limitations of this technique are discussed in Section 4 in the subsection entitled Carbon Aerosols.

Millipore Fluoropore filters (47 mm diameter, 0.5 μm pore size) were used to collect aerosol samples for sulfate and nitrate analyses. These filters produced minimal sorption of SO_2 and artifact sulfate formation and also facilitated analysis by XRF. Generally, duplicate aerosol samples were obtained, with one of the samples being drawn through a heated inlet ($\sim$65° C). The heated aerosol sample was first analyzed by non-destructive XRF (for elemental sulfur) and then the extract analyzed by ion chromatography (for sulfate). The unheated samples were analyzed only by ion chromatography (for sulfates and nitrates). All samples were 'fixed' with exposure to NH_3 prior to storage and analysis.

Carbon samples were collected upon 47 mm quartz fiber filters (Pallflex QAST). After sampling, the filters were placed in specially prepared, aluminum lined petri dishes. Aluminum lining was necessary to prevent possible contamination during storage and shipment.

A system of three hi-vol samplers (Model HP33 Cadillac Blowers) was installed in the chamber to provide large quantities of aerosol for mutagenic testing. The system was recirculatory in nature, exhausting the filtered air back into the chamber. This method provided a closed filtration system minimizing the possibility of contamination. Approximately 60% of the chamber aerosol could be filtered in three hours of sampling with an initial flow rate of about 10 m^3/min (unloaded filters), providing a sample mass on the order of 0.1 gm. The samples were collected upon 8 x 10 inch glass fiber filters (Pallflex T60A20). For the latter series of tests (experiments 31-60), the filter samples were wrapped in aluminum foil, previously cleaned with methylene chloride, to prevent possible reactions involving the organic carbons. All samples were shipped to EPA's Health Effects Research Laboratory for mutagenic testing by the standard Ames test.